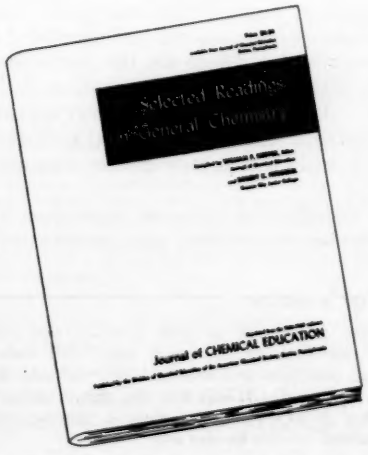
Chem Ed

EDITORIALLY SPEAKING

Requests for reprints of my article have exhausted the original 400 ordered and are continuing to flow in." . . . "I have never had as much call for reprints of any article that I have published." "Requests have come from 28 states and 13 foreign countries." ". . . as many are coming from industry as from the academic world." —So write our authors.

Letters such as these have prompted the decision to publish "Selected Readings in General Chemistry," a 128-page collection of over 40 papers which have appeared in dozens of separate issues during the last three years. On the list of authors, such names as Calvin, Libby, Nyholm, Pauling, and Williams are recognized by chemists everywhere. Topics range from spontaneous generation of life to solid state models, and from antiknock quality in gasoline out into space with the IGY and amateur rocketry. Obvious economies of production dictated a fitting together of material as it appeared originally on the pages of the JOURNAL OF CHEMICAL EDUCATION. Except for Chem-Gems and minor articles scattered through as "filler," an attempt has been made to suggest a continuity by sequence of articles. Readers will find a complete Table of Contents on page A119 of this issue.



The term "General Chemistry" is a purposeful choice; it implies no narrow range of topics. In fact, we feel that the articles reprinted here are among the best examples of the type that the JOURNAL OF CHEMICAL EDUCATION, often called a "living textbook of chemistry," tries constantly to provide: discussions written by the specialist for the informed nonspecialist.

For many, the convenience of having reprints of even a few of the titles will be worth the modest price of $2 per copy. Others will see the volume as an ideal collection of reference material for classes and will take advantage of the quantity discounts. Many who are looking for an award to maintain scientific excitement in winners of student contests will find this volume appropriate. It is part of the plan for the book that the final material has an obvious vocational guidance intent.

We have an even more specific purpose in mind, however. We want to provide a volume which will aid in promoting the most significant development in chemical education: a large-scale emphasis on the subject-matter competence of those trained for secondary school chemistry teaching. Events of recent years, backed up by the planned provision of training programs such as those sponsored by the National Science Foundation, have developed many enthusiasms for chemistry as a living science. We hope the contents of these pages will reinforce these enthusiasms.

Good teaching in a chemistry classroom demands, first of all, knowledge of chemistry. At least three-fourths of this volume emphasizes this by providing *chemical* information. Newest developments in the research laboratory and the correlating theories are more than "news" for the chemistry teacher. They are a necessary store of knowledge from which he can draw illustrations to make even the simplest chemical principles come alive for his students. Another portion of this volume contains descriptions of laboratory experiments. The selection of these likewise makes an emphasis: Chemistry is an experimental science. The student should anticipate his laboratory as exciting "research," not as dull exercises confirming what the text tells him will happen. Our selection includes experiments which we hope are unique, not because of the manipulations described, but because they should suggest to the reader that he use his own ingenuity to devise new ways of doing familiar operations.

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Explosive Hazard of Aluminum-Liquid Oxygen Mixtures

Since its original description in 1931 by Cady (*6*) as a "safe, sure, and easy to perform" lecture demonstration experiment, the use of powdered aluminum-liquid oxygen mixtures to demonstrate vigorous oxidation of metals in a high concentration of oxygen has found its way into at least two widely used reference books on demonstrations for general and high school chemistry (*2, 13*). In none of these accounts is the explosive power of this reaction and the extreme hazard involved made clear. Consequently the experiment has been used by numerous demonstrators without realization that they were subjecting themselves and their audiences to the danger of severe and possibly fatal injury.

On April 24, 1957, this experiment was performed in the Indiana University Chemistry Auditorium before approximately 200 visiting high school students and adults. Contrary to its behavior in many previous demonstrations, the aluminum-oxygen mixture detonated instead of producing the bright but harmless flare (*15*). Fragments of two iron dishes and part of a stone tabletop were hurled throughout the auditorium. The severity of the explosion is most vividly revealed in the casualties, which ranged from the loss of an eye, a crushed bone in one arm, very severe face and body lacerations, and a broken ear drum, on down to minor scratches. The heavy stone top of one section of the lecture demonstration table was demolished. The experiment had been performed many times by the demonstrator, several colleagues, and numerous acquaintances, yet none apparently realized the hazards involved.

In the past, lampblack impregnated with liquid oxygen has been used as an explosive. Perrott and Tolch (*10*) investigated such explosives. In a few tests they mixed a small amount of powdered aluminum with the carbon, noting no significant effect. Davis (*7*) briefly mentions the use as explosive of liquid oxygen impregnated cartridges of porous combustible material. Such explosives are members of the general class of Sprengel (*11*) explosives. Davis attributes the explosive power of confined spongy metallic aluminum and liquid oxygen to the "extremely rapid gasification of the excess of liquid oxygen" resulting from the heat of oxidation of the aluminum. In an unpublished master's thesis Bruce (*5*) describes experiments on the detonation of mixtures of aluminum powder and liquid oxygen in an open dish. Kirshenbaum (*9*) recently discussed the explosion of confined aluminum-oxygen mixtures in a report to the Office of Ordnance Research.

In none of the above reports that were published in the literature available in the average library is there any indication that aluminum and liquid oxygen could detonate under the conditions of the experiment. Yet, since the first announcement of the explosion at Indiana University there have been reports of at least six similar explosions at other schools during the past 25 years (*1, 3, 4*); and Grosse (*8*) has discussed the dangers associated with liquid oxygen. To avoid future accidents with this experiment every person reading this article should make certain that a marginal note is inserted in each copy of (*2*), (*6*), and (*13*) in his personal and departmental libraries, informing future readers that this experiment is extremely dangerous and directing them to this report.

To answer questions raised by the April 24th explosion, experimental work was done in the barricaded cells of the Quality Evaluation Laboratory, Naval Ammunition Depot, Crane, Indiana. The results of this work are presented and discussed in this report. A brief summary of the thermal theory of explosions is also presented.

Experimental

At the Quality Evaluation Laboratory reinforced concrete cells with steel doors are available and these were used for all experiments. The general procedure was to place aluminum powder in an iron crucible contained in a larger iron dish half full of sand. If liquid oxygen is poured on warm powder a large fraction is spattered from the crucible by the boiling oxygen. Therefore liquid oxygen was first poured on the sand to precool the aluminum and minimize loss of metal. An excess was then added to the aluminum. Except as noted in Table 1, evaporation was permitted to proceed until no liquid oxygen was visible and the still moist aluminum had cratered and resembled a pancake ready for turning. These are the conditions for ignition specified in the original description of this experiment (*6*). At this point the observer quickly left the cell and the combustion was initiated as described below instead of with the lighted candle recommended by Cady.

Three initiators of different intensities were used. These were squibs, igniters, and hot wires. The squib

Editor's note

The cover photograph is grim evidence that unexpected tragedy can occur on the lecture table. We hope that all librarians will turn to Volume 8 (1931) of THIS JOURNAL, *mark a big red* DANGER *over the picture which appears at the top of page 1040, and make a reference note to the article which appears on this page.*

[1] Present address: East Texas College, Commerce, Texas.

is a small brass cap loaded with black powder, totally enclosed, and electrically ignited, which gives a small explosion producing both flame and shock. The igniter is a small charge of black powder initiated electrically but unenclosed so that a short spurt of flame and negligible shock is produced. For hot wire ignition, 10 cm of standard Parr bomb fuse wire and the Parr ignition unit were used. These methods of ignition were believed to be in the order of decreasing initiating power and this belief was borne out by experiment.

Since a portion of aluminum powder taken from the same bottle used in the April 24th demonstration at Indiana University was found to contain 0.2% by weight of ether-extractable material, there was some question as to the influence of organic impurities on the ease of detonation. Therefore, trials were made both with the original aluminum powder and with powder that had been well washed with ether. Since no significant differences in behavior were found, they are treated as identical samples in this report. In some of the hot wire ignitions a small pellet of candle wax was pressed around the wire at the point closest to the aluminum. This had no noticeable effect and these trials are not differentiated from the others. For most of the experiments 25 ml of aluminum powder (9 to 10 g) were used in the crucible. The upper surface of the aluminum was about 1.5 inches in diameter. In a few experiments either 10 or 50 ml of powder were used. In seven experiments 50 ml of powder were spread over sand in a 6-inch diameter hemispherical iron dish (diameter of sand surface = 4 inches). The small difference in behavior that was observed for the few 10- and 50-ml samples cannot be considered significant in view of the variation in behavior of the 25-ml samples. Significant variations were observed for the three different methods of initiating the combustion. The experimental results are summarized in Table 1.

Table 1. Results of Firing Aluminum-Liquid Oxygen Mixtures with Different Initiators

Initiator	Number of Ignitions	Results
Squib	8	4 high order detonations[a] 2 low order detonations[b] 2 flares
Igniter	5	1 high order detonation following approximately 2-sec flare 1 low order detonation preceded by brief flare, a low order detonation, and a longer flare 3 flares
Hot wire	13	3 high order detonations following approximately 2-sec flares 1 low order detonation preceded by a brief flare, a low order detonation, and another brief flare 9 flares

[a] No perceptible period of combustion preceded the detonations. Two of the mixtures were ignited at the time recommended in the original description of the experiment (*6*); one was ignited 30 sec after the recommended time; the fourth was ignited while excess liquid oxygen was still present above the aluminum.

[b] Due to loss of aluminum by boiling oxygen less than 10 ml of powder were ignited. No perceptible period of combustion preceded the detonations.

For interpretation of these results a definition of terms is advisable. Inasmuch as precise measurements were impractical these definitions are necessarily subjective and empirical. *Flare* designates a vigorous reaction emitting heat and light and lasting an appreciable time, of the order of seconds. What we have called a *low order detonation* with aluminum-liquid oxygen mixture is more probably an extremely rapid deflagration, with a probable duration of the order of milliseconds, with an appreciable local pressure rise, and the production of a dull bang somewhat similar to the explosion of confined black powder. It was differentiated from the high order detonation primarily by damage done to the iron crucible, the former damaging it slightly or not at all. A *high order detonation*, on the other hand, is a true detonation with probable duration, for the amount involved, of a few microseconds. The shock wave and blast effects here are typical of those produced by conventional high explosives such as nitroglycerin or trinitrotoluene. In all cases of high order detonation the crucible was completely shattered and the iron sand-bath container either shattered or distorted beyond reuse.

Discussion

As has been pointed out elsewhere (*8*, *9*) the energy release of the aluminum-liquid oxygen explosion is 3.85 times that of an equal weight of TNT. Whether a harmless flame or a dangerous detonation occurs depends on the time required for the energy to be released and therefore on the rate of reaction. Since the chemist deals with many exothermic reactions, some of which are potentially dangerous, it should be profitable to consider briefly a few of the factors that contribute to detonation and some characteristics of explosives. It will be seen that the behavior of aluminum-liquid oxygen mixtures corresponds to that of other more common explosives.

In his monograph, *Detonation in Condensed Explosives*, Taylor (*12*) states: "Strictly speaking, the fundamental difference is between burning and detonation, not between explosive substances themselves, for it is quite common to find that an explosive can either burn or detonate according to the method of initiation or the quantity of material involved. If the mass of explosive is small, thermal ignition usually, if not always, leads to burning, but if the mass exceeds a critical value it is possible for burning to become so rapid that it sets up a shock wave-front and detonation ensues."

Detailed studies of explosives utilize the hydrodynamic theory of detonation (*12*), which relates the velocity of the detonation wave, the detonation temperature and pressure, the volume of the products, and their streaming velocity behind the wave-front. Only the chemist studying explosives need be concerned with an analysis of what occurs in the detonation wave. The majority of chemists, however, need be concerned only with avoiding detonation and therefore with the fact that for any given set of conditions there is a critical temperature required to produce and maintain a detonation wave. Since some of the factors that contribute to the production of this required temperature are studied in the undergraduate courses in physics and physical chemistry, it is certainly desirable that each instructor, for the future safety of his students, show at least qualitatively the relation of factors influencing heat transfer and rate of reaction to the danger of detonation in the case of exothermic reactions.

The rate of all exothermic reactions can be represented by the equation

$$r = \kappa e^{-E/RT} \quad (1)$$

where r is the rate in terms of the fraction of the material at temperature T that reacts per unit time, E is the activation energy per mole, and R is the gas constant. κ is a function of one or more of the following: the temperature, the concentration of reactants, and their state of subdivision or surface area per gram. Equation (1) obviously involves the Arrhenius equation, the relationship of reaction rate to concentration, and the relationship between total amount of reaction at an interface and the area of interface. The heat conduction equation is

$$-\lambda\nabla^2 T + c\rho\frac{\partial T}{\partial t} = B \quad (2)$$

where λ is the thermal conductivity, c is the specific heat, ρ is the density, t is time, and B is the energy input per unit volume and unit time. When the source of energy is a chemical reaction,

$$B = r\rho q \quad (3)$$

where q is the heat of reaction per gram. The second term in equation (2) equals the absorbed energy, which causes increase in temperature. The first term is the remaining energy, which is lost to the surroundings. If significant energy is lost by convection or radiation, additional terms must be added. The total energy lost to the surroundings increases with increasing temperature gradient between the source of heat and the surroundings and is also proportional to the thermal conductivity of reactant, products, and other materials present. The thermal conductivity of powders, such as aluminum, is a function of particle size, degree of packing, and presence of cracks in the packed mass. If the total loss of energy to the surroundings per unit time, which would be a complex function of the numerous factors mentioned above, is represented by Q, then

$$B = \rho q\kappa e^{-E/RT} = c\rho\frac{\partial T}{\partial t} + Q \quad (4)$$

where it must be understood that the specific heat c includes latent heat of any phase transition for reactants, products, or diluting inert material. B increases rapidly with increasing temperature. As long as Q is equal to or greater than B the temperature does not rise. If, however, B is greater than Q the temperature will rise and continue to do so until B and Q become equal. If this does not occur before the critical temperature for detonation is reached, a shock wave-front results.

Even from the above simplified discussion it is readily seen that the probability of detonation is influenced by many factors. Since inhomogeneities, degree of packing, presence of small fissures, and other factors cannot be duplicated exactly in successive samples of an explosive it becomes necessary to make a statistical study of the probability of explosion under different conditions. This is done in the determination of the "sensitiveness" or "sensitivity" of an explosive, which indicates the ease of detonation. Various methods have been used to measure sensitiveness, the most widely used test being that of impact sensitivity (*14*). This test consists of dropping a standard weight from variable heights onto a hardened steel striker which in turn crushes a small (usually less than 50 mg) sample of the explosive under test between it and a hardened steel anvil. Many of the parameters involved in impact testing are not well understood and good agreement among the results obtained by different laboratories is seldom achieved. The results with any one explosive on the same equipment are not reproducible between individual determinations. Therefore it is impossible to find a single impact value above which detonation always occurs and below which it never occurs. However, when a large number of trials are made at each height the percentage of samples detonating indicates a probability of detonation for the given impact. As sample uniformity is improved and the number of samples is increased the resulting probability of detonation becomes a reproducible quantity for an explosive under any given impact conditions. When the percentage of explosions is plotted against the height of fall, a curve is obtained similar to those shown in Figure 1 for two explosives. Under the conditions for which these curves were obtained the probability of detonation for TNT varies from approximately 0 at 55 cm to practically 100% at 105 cm with 50% probability at about 80 cm. Amatol, on the other hand, with a 50% point at about 100 cm is apparently the less sensitive. Even the 5% points are at 69 cm and 71 cm, respectively. At the 1% level, however, TNT requires a 60-cm drop while the generally less sensitive amatol will detonate, again at the 1% probability level, with a drop of only 50 cm. Although it is not shown by the curves, it is apparent that the probability of explosion at the 0.01% level would be at an appreciably lower height.

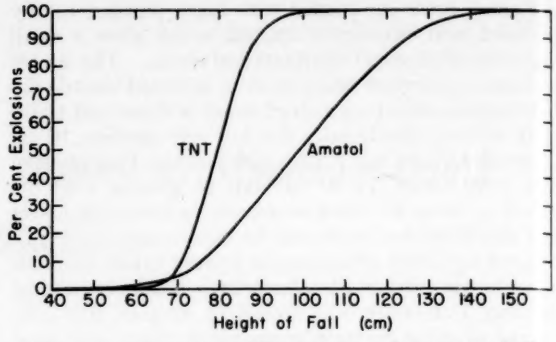

Figure 1. Impact sensitivity of TNT and Amatol [after Wright (*14*)].

The above brief discussion of impact sensitivity is of general application to other forms of initiation, the probability of detonation varying according to the "strength" of the initiator. As shown by the data in Table 1, this applies to aluminum-liquid oxygen mixtures. We see that with an initiator of considerable power, the squib, the probability of immediate detonation is high. When the hot wire method of initiation was used detonation occurred only after preliminary simple combustion. We might note here that several witnesses to the explosion which led to this investigation stated that there was an observable period of combustion prior to the actual detonation. With hot wire ignition the initial temperature of the reacting mixture is apparently below the critical temperature for detonation, but detonation can result if, under the pre-

vailing conditions, heat from the reaction exceeds heat loss to the surroundings.

Bruce (*5*), who ignited aluminum-liquid oxygen mixtures with an acetylene flame, consistently observed detonation with mixtures containing enough liquid oxygen to oxidize 83% to 90% of the aluminum and observed weak explosions and flares outside this concentration range. When igniting the mixture by a spark discharge he obtained consistent detonation for a wider range of concentrations, from a liquid oxygen deficiency of 12% to an excess of 10%. Since the effect of dilution with excess reactant was more apparent with acetylene flame ignition than with ignition by spark discharge, the "strength" of initiation by the latter must exceed that of the acetylene flame. Since Bruce may have used different particle size, weight of sample, and depth of aluminum layer than were used in this investigation, the "strength" of his methods of ignition cannot be compared with those listed in Table 1.

Barker (*3*) states that he experienced an explosion of aluminum-liquid oxygen after successfully performing the experiment about three times per year for a period of ten years, always obtaining a flare. After subsequent experimentation he concluded that explosion will result from packing of the aluminum powder by tapping the container. Packing of the powder affects both ρ and λ (Eq. 2) and probably also influences the relative amounts of aluminum and liquid oxygen present when the mixture has the appearance described by Cady as indicating the time for ignition. Adams (*1*) experienced an explosion after at least six successful demonstrations producing flares. The investigation of aluminum-liquid oxygen as an explosive by Bruce (*5*) followed the explosion experienced by Bawden (*4*) after about 100 successful demonstrations of the flare. The explosion at Indiana University occurred after at least 20 successful combustion demonstrations in the department by three different demonstrators. Doubtlessly Cady and others have performed the experiment many times without producing a detonation.

The above indicates a low order of probability of detonation when the mild initiating conditions described by Cady are used. However, there is a definite possibility of explosion.

Conclusion

The aluminum-liquid oxygen mixture must be considered a high explosive. Ignition of this mixture by candle flame, as originally described (*6*), probably in no case causes immediate detonation. However, as shown by this investigation and by the unfortunate experiences of a number of demonstrators, the combustion itself can create the critical conditions that produce detonation. Because of the many variables involved and the difficulty of controlling them, no one can with certainty carry out this combustion with no danger of detonation. These statements apply equally to any experiment involving a mixture of liquid oxygen and oxidizable materials. For example, as pointed out by Grosse (*8*), a mixture of alcohol and liquid oxygen (*6*, p. 1032), if properly initiated, can be made to detonate like dynamite. Though the probability of detonation may be low with small amounts of aluminum or other oxidizable material and with mild initiating conditions, it is not zero and therefore these experiments should NEVER be used for classroom or public demonstration unless facilities are available to demonstrate safely the detonation of any high explosive.

Literature Cited

(1) Adams, C. S., Private communication to H. G. Day.
(2) Arthur, P., "Lecture Demonstrations in General Chemistry," McGraw-Hill Book Co., Inc., New York, 1939, p. 232.
(3) Barker, J. W., Private communication to H. G. Day.
(4) Bawden, A. T., *Chem. Eng. News*, **35**, No. 31, 11 (Aug. 5, 1957).
(5) Bruce, D. S., "Explosive Property of Aluminum Powder Liquid Oxygen Mixture," M.S. Thesis, College of the Pacific, 1936.
(6) Cady, H. P., J. Chem. Educ., **8**, 1040 (1931).
(7) Davis, T. L., "The Chemistry of Powder and Explosives," John Wiley & Sons, Inc., New York, 1943, Vol. II, p. 356.
(8) Grosse, A. V., *Chem. Eng. News*, **35**, No. 31, 9 (Aug. 5, 1957).
(9) Kirshenbaum, A. D., "Final Report on Fundamental Studies of New Explosive Reactions for Office of Ordnance Research," Contract No. DA-36-034-ORD-1489, Research Institute of Temple University, Philadelphia, April 30, 1956.
(10) Perrott, G. St. J. and Tolch, N. A., "Liquid Oxygen Explosives," United States Bureau of Mines Bulletin No. 349 (1932).
(11) Stettbacher, A., "Spreng- und Schiesstoffe," Racher and Co., Zurich, Switzerland, 1948, p. 71.
(12) Taylor, J., "Detonation in Condensed Explosives," Oxford University Press, London, 1952, pp. 1–2.
(13) Weisbruch, F. T., "Lecture Demonstration Experiments for High School Chemistry," Educational Publishers, Inc., St. Louis, 1951, p. 152.
(14) Wright, G. F., "Chemistry of Explosives," Chapter 10 in Gilman, H., "Organic Chemistry," John Wiley & Sons, Inc., New York, 1953, Vol. IV, pp. 962–5.
(15) "Experiment Explodes," *Chem. Eng. News*, **35**, No. 24, 90 (June 17, 1957).

More Mnemonics

For the transitional elements:

Period Four: "Saint Thomas very carefully made five completely new copies of Zarathustra."
(Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn).

Period Five: "Your xylophone needs more tuning. Remember Robert played arpeggios clandestinely."
(Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd).

Period Six (Exclusive of the Lanthanide Series): "H. T. Walker read Oglethorpe's inimitable 'Principles of Agriculture and Horticulture'."
(Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg).

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Instability of Sulfur-Potassium Chlorate Mixture

A chemical view

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Numerous amateur rocket enthusiasts suffered serious casualties from premature sulfur-chlorate[1] explosions, according to C. Burns (*1*). This is most regrettable. These accidents should challenge elementary chemistry teachers, textbook writers, and civic-minded chemists to do their utmost to teach safety to tyro chemists. Chemistry without safety is too frequently fatal.

The following exposition of the chemistry of sulfur-chlorate mixture is presented with the hope that the information will be conveyed to secondary school chemistry students as a lesson in safety. Safety is not a series of "don'ts," but is a matter of foresight with avoidance of hazards. In the discussion of the chemistry of sulfur-chlorate mixture, an example of how safety can be designed into an experiment is included for the benefit of the chemists of tomorrow.

Sulfur, by itself, is not a particularly reactive element at ambient temperatures. Even in the finely divided state it is difficult to ignite. Similarly, chlorate is a relatively stable compound at ordinary temperature. It decomposes only when heated (*2*) almost to its melting point of 368°C. It is much less reactive at room temperature than is pure oxygen, for example. These facts would not incline one to predict that a simple mixture of sulfur and chlorate might ignite spontaneously after being stored in a warehouse many months, or detonate when a fuse is being stuffed into a rocket charge.

World accident records for the past century show that sulfur-chlorate stability is erratic and unpredictable. This fact indicates that the mixture might contain a concealed chemical trigger. A close look, particularly at sulfur, discloses this trigger and the manner in which it becomes cocked.

There are two basic grades of sulfur—crude and refined. Sulfur produced at the mine is called crude sulfur (formerly "roll sulfur"). About half of the world supply of sulfur is extracted from the ground in Texas by the Frasch process. Traditionally, this raw product is called crude sulfur, even though it has the amazing purity of 99.8 to 99.9% sulfur. The chief impurity is asphalt which is present in the dissolved state. This mere trace of asphalt makes raw sulfur difficult to burn on a large scale. Air oxidation at ordinary temperature is detectable only after a period of months. Moisture in the air assists this slow "rusting" process.

Refined sulfur is produced by distillation. The purest is obtained under conditions that cause the sulfur vapor to condense directly to the solid state, i.e., the sulfur is sublimed. The product, called flowers of sulfur, when freshly prepared has an average purity of 100.0% sulfur. Even when both grades of sulfur are pulverized to the same degree of fineness, flowers of sulfur oxidize more rapidly because its surface is cleaner.

[1] Throughout this paper, chlorate will refer to potassium chlorate.

Polythionic Acid, the "Trigger"

Air oxidation probably produces sulfurous acid on the surface of sulfur, but this acid has not been detected (*3*) because, as H. Debus (*4*) showed, sulfurous acid reacts quickly with sulfur to form polythionic acids beginning with trithionic acid, $H_2S_3O_6$. The latter adds sulfur atoms successively to form tetra- and pentathionic acids. These acids, particularly pentathionic acid (*5*), are responsible for the fungicidal value of dusting sulfurs. Aqueous polythionic acids accumulate until the concentration reaches a limit (*6*) where evaporation or a temperature rise will cause partial decomposition according to the equation:

$$H_2S_nO_6 = H_2SO_4 + SO_2 + (n - 2)\,S \qquad (1)$$

The reaction is irreversible, but loss of polythionic acids becomes repaired by air oxidation of sulfur when the temperature subsides. Reaction (1) is significant in that a sudden increase in temperature can cause a significant amount of sulfur dioxide to be formed, not by direct oxidation of sulfur, but by decomposition of a concentrated solution of polythionic acids. This event, however, must await the formation of a concentrated solution of these acids.

Reaction (1) is responsible also for the accumulation of sulfuric acid on sulfur. The sulfuric acid, being hygroscopic, favors additional production of polythionic acids. By capillary action, sulfuric acid coats the surface of chlorate and produces chloric acid. Although dilute chloric acid at ambient temperature is a very weak oxidizing agent, its presence has given rise to the theory that chloric acid is the primary cause of sulfur-chlorate instability.

Sulfur dioxide will react directly with moist chlorate to produce chlorine dioxide.

$$SO_2 + 2KClO_3 = 2ClO_2 + K_2SO_4 \qquad (2)$$

Chlorine dioxide immediately attacks sulfur, the chief reaction being,

$$2ClO_2 + 4S = 2SO_2 + S_2Cl_2 \qquad (3)$$

Expressing reactions (2) and (3) as one reaction,

$$SO_2 + 2KClO_3 + 4S = 2SO_2 + S_2Cl_2 + K_2SO_4 \qquad (4)$$

Reaction (4) is a chain reaction because more sulfur dioxide is produced than is consumed. Initiation of reaction (4) requires an extraneous source of sulfur dioxide. This is furnished by reaction (1) which is, therefore, the trigger reaction. The trigger is cocked by the growth of polythionic acids on the sulfur, and is

"pulled" when the heat from friction, impact, sunshine, and the like is sufficient to release a threshold amount of sulfur dioxide from the "reservoir" of polythionic acids. Heat from reaction (4) quickly ignites a portion of the mixture, and, if the gases produced cannot escape readily, the mixture will explode.

Popular formulas for preparing sulfur-chlorate mixtures generally specify more sulfur than can be oxidized by the chlorate to sulfur trioxide. The reasons for this are not pertinent to this subject, but it is important to note that the excess sulfur increases the instability of the mixture by favoring formation of a greater amount of polythionic acids.

This "trigger" theory was capable of explaining some previously baffling industrial accident conditions, but it needed experimental confirmation. It predicted that a chlorate mixture prepared with an oxidation-resistant crude sulfur would be more stable than one prepared with flowers of sulfur. Comparative tests were made using ignition temperature as an index of stability.

Experiment A: 2 g of flowers of sulfur, 4 g of reagent grade chlorate, and 4 g of cleaned and dried sand were intermingled on unglazed paper with a metal spatula; 1 ml of water was added dropwise, and the mixing was continued. The product was pressed lightly into a thin open-ended cardboard tube made from a paper match-cover after the striker strip had been cut off. The tube was laid on an asbestos board in an empty ventilated hood and was heated at approximately 1°C temperature rise per minute by a heat lamp suspended above the tube. The temperature was measured with a thermocouple inserted to the center of the mixture. Ignition temperatures on repeat experiments ranged from 82 to 91°C, and averaged 85°C.

Safety precautions that were designed into the above experiment include mixing the powders with a metal spatula and the use of unglazed paper to reduce accumulation of static charges. The powder was dampened primarily to give it sufficient cohesion to remain in the cardboard tube, but the dampness no doubt helped to suppress static charges. The striker strip was removed from the match-cover because it contains a sulfide of phosphorus which might ignite the mixture prematurely by contact with stray chlorate. Porosity, contributed by sand, and the short open-ended tube all owed easy escape of gases, thereby reducing the probability of an explosion. Both ends of the tube were left open to reduce fire hazard by canceling rocket effects when the mixture ignited. Fire hazard was further reduced by the asbestos board and by the emptiness of the hood.

Experiment B: Mixtures similar to those in Experiment A were prepared with crude sulfur that had been pulverized until the particles had a mass median diameter of 44 microns, thereby approximating the particle size of flowers of sulfur. These mixtures ignited sharply at 124°C. This temperature is above the melting point of sulfur and indicates that ignition may have been initiated by sulfur dioxide produced by air oxidation of hot sulfur vapor.

Experiments A and B definitely demonstrated the predicted greater stability of the crude sulfur mix. However, the chloric acid theory could predict that the greater sulfuric acid content of the flowers of sulfur, instead of the polythionic acids, would cause the lower ignition temperature. As a matter of fact, the flowers of sulfur contained 0.02% "acidity" calculated as sulfuric acid. The acidity of the crude sulfur was detectable but was too small to titrate.

As a test of the "chloric acid" theory, Experiment A was repeated using flowers of sulfur dampened with sufficient 0.2 *N* H_2SO_4 to give it an acidity value of 0.50%. When this highly acidified sulfur was mixed with chlorate, an abnormal amount of chloric acid must have been formed. In spite of this excess, the ignition temperatures averaged only 87°C in close agreement with Experiment A. These results dismiss the "chloric acid" theory as a primary explanation of instability.

Final confirmation that sulfur dioxide triggers the ignition was obtained by repeating Experiment A, but, instead of heating the mixture, a long capillary glass tube containing sulfur dioxide flowing at the rate of 0.3 cc per second was thrust into the mixture. Ignition occurred almost as quickly as though the flame of a match had been applied.

Sulfur-chlorate typifies many fuel-chlorate mixtures. Metallic sulfides and polysulfides behave qualitatively like sulfur. Phosphorus cannot yield sulfur dioxide, but at room temperature it evolves reducing vapors of phosphorus oxide and possibly some elemental phosphorus which react so energetically with chlorate that an explosion usually occurs before mixing can be accomplished. Carbon disulfide, rosin, turpentine, thiocyanates, aldehydes, sugars, tannin, and numerous other materials that form volatile reducing agents on heating, contribute instability to chlorate mixtures. Powdered metals such as oily aluminum, zinc, and magnesium are sometimes used with or without other fuels in chlorate mixture. These metals are corroded by chlorate. Their chlorates are hygroscopic and decompose at relatively low temperatures. The high heats of oxidation of these metals could cause local temperatures sufficiently high to ignite the mixture. No wonder such concoctions are unpredictable in stability.

Much of the unsavory reputation assigned to chlorate should be reassigned to those who have selected the fuels. Apparently availability and cheapness, instead of chemistry, have dictated the choice of fuels. Any fuel that is subject to air oxidation at ordinary temperature, or forms an unstable chlorate, or produces an easily oxidizable vapor below 100°C, or reacts with chlorate below 150°C should be excluded. Starch (7) is a fuel that survives these requirements.

Literature Cited

(1) Burns, C., J. Chem. Educ., **33**, 508 (1956).
(2) Brown, F. E., and White, W. C. O., *Proc. Iowa Acad Sci.*, **31**, 291 (1924).
(3) Mellor, J. W., "Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans, Green & Co., Inc., London, **1947**, Vol. 10, p. 88.
(4) Debus, H., *Ann.*, **244**, 76 (1888).
(5) Young, H. C., and Williams, Robert, *Science*, **67**, 19 (1928).
(6) Mellor, J. W., "Modern Inorganic Chemistry," Longmans, Green & Co., Inc., London, **1916**, p. 458; Ephraim, Fritz, "Inorganic Chemistry," Gurney and Jackson, London, **1926**, p. 463.
(7) Tanner, H. G., U.S. Patent 1,966,652 (1934).

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Transformation of Organic Compounds by Microorganisms

During the past quarter century an increasing number of chemists have been employing microorganisms to carry out desired changes in organic molecules; changes which in many instances can be accomplished only with considerable difficulty by the standard techniques of organic chemistry. It is the purpose of this review to classify some of the transformations in which microbial processes have been of some use, and to indicate some of the practical limitations which have been encountered. This discussion will be confined to those changes where the basic structure of the molecule is left intact and will not mention the purely synthetic microbial activities. As the literature is voluminous and space is limited, only twelve types of transformations will be mentioned and only a few examples will be presented. Other examples of the types of transformations mentioned in the following pages can be found in the summary prepared by Stodola (*1*). Information on the mechanisms of the reactions and possible intermediates can be found in the monographs by Gale (*2*) and by Oginsky and Umbreit (*3*).

The types of chemical reactions carried out by microörganisms which will be discussed include:

(1) *Oxidations* where oxygen is added to the molecule or hydrogen is removed.
(2) *Reductions* where hydrogen is added to the molecule or oxygen is removed.
(3) *Specific hydrolyses* where water is added to a certain linkage followed by splitting of the molecule.
(4) *Decarboxylation* where carbon dioxide is eliminated from the molecule.
(5) *Deamination* where amino groups are removed from the molecule resulting in formation of a keto acid (oxidative deamination), formation of a double bond (desaturation), or replacement with hydrogen (reductive deamination).
(6) *Amination* where an amino group is introduced into the molecule.
(7) *Phosphorylation* where phosphate esters are added directly to the molecule.
(8) *Transfer reactions* where glycoside residues, amino acid residues, or phosphate residues are transferred from one molecule to another without apparent participation of water in the reaction.
(9) *Racemization* where optically active compounds are converted into the enantiomorphs.
(10) *Dehydrations* where water is eliminated from the molecule.
(11) *Demethylation* where a methyl group is eliminated from the molecule.
(12) *Condensations* where two aldehydes are joined.

Examples of these types of modifications of organic compounds by microorganisms and simplifications of the chemistry involved are presented in Table 1. Many of these examples represent processes which have gained industrial importance, and these are marked by a footnote in the table. Among these are the following oxidations: the conversion by bacteria or *Aspergillus niger* of glucose to gluconic acid is a process used for the annual production of about 2500 tons of the acid; the conversion by *Acetobacter suboxydans* of sorbitol to sorbose, a sugar used as an intermediate in the production of the nearly 1000 tons of ascorbic acid produced every year; the introduction of the hydroxyl function in the 11 position of the cyclopentanophenanthrene nucleus by a number of fungi including *Rhizopus nigricans* and *Curvularia lunata* resulting in intermediates used in the production of thousands of pounds of hydrocortisone; and the conversion of hydrocortisone to prednisolone by bacterial action. Hydrolyses important in the food industries are those which use microbial enzymes including the processes where sucrose is inverted to fructose and glucose, starch is hydrolyzed to maltose and to dextrins, lactose is hydrolyzed to galactose and glucose, and dextrins are hydrolyzed to maltose. Of more interest to the practical organic chemist are the hydrolyses catalyzed by enzymes including the splitting of N-acetylated L-amino acids (but not acylated D amino acids) by fungal acylase (*39*) and the conversion of saponins to diosgenin by fungal enzymes (*19*). The production of lysine by microbial decarboxylation of diaminopimelic acid has recently assumed commercial importance, as has a process for the production of glutamic acid where microbial amination of α-ketoglutaric acid is the important step. Practically all of the L-ephedrine produced for medicinal purposes is made by a process in which yeast is used to condense benzaldehyde with acetaldehyde to form phenylacetylcarbinol which in turn is converted to L-ephedrine by catalytic reduction with methyl-amine. Undesired microbial transformations which are of some concern to the chemist are the conversion of glycerol to acrolein (accounting for the "peppery" taste of some whiskies), and the racemization of lysine and lactic acids as a result of microbial enzymes produced by contaminating bacteria in fermentation processes used for the production of these chemicals.

While some of the other transformations mentioned in Table 1 have reached commercial scale, many of them have been of more interest to the chemist in preparing new compounds. The recent interest in the relationship of structure to biological activity in the corticosteroid series has resulted in many reports on the microbial transformations of these rather complex organic molecules. Among the oxidations reported are processes for the introduction of hydroxyl groups in

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positions 1α, 2β, 6β, 7α, 8, 9α, 10, 11α, 11β, 12β, 14α, 15α, 15β, 16α, 17α, 19, and 21 of certain pregnene derivatives, and removal of hydrogen from position 1 (2). Microorganisms can also be used to remove side chains (leaving a hydroxyl) or to insert an oxygen into the D ring as well as to oxidize a hydroxyl to a ketone or reduce a ketone to a hydroxyl. These microbial systems often have remarkable stereospecificity and oxidize or reduce only the D isomer when presented with a D, L mixture. This specificity was used by Vischer (*40*) in his process for the synthesis of the biologically important steroid, aldosterone. A consideration of these and other problems encountered in studying microbial modification of steroids is the subject of an extensive review by Eppstein *et al.* (*41*).

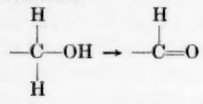
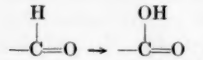
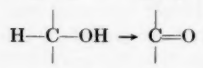
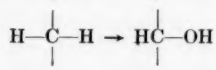
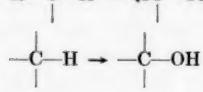
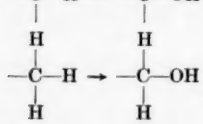
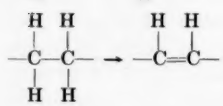
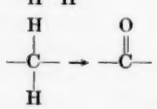
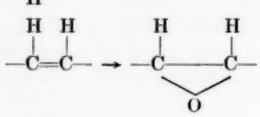
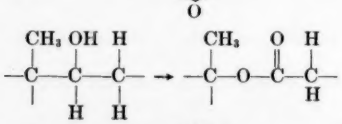
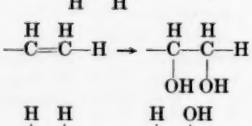
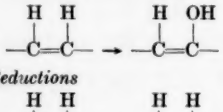
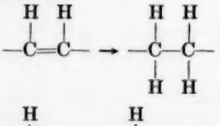
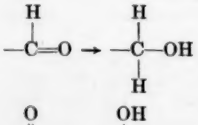
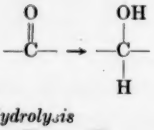
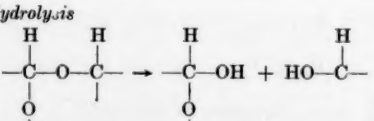
In studying the use of microorganisms to transform organic substances a certain amount of knowledge of the techniques of microbiology is needed. If the interest lies in reproducing results reported from other laboratories, care must be exercised in carrying out the fermentations exactly as described using the same strain of microorganism, conditions, and medium for growth of microorganism, and recovery of the desired material. Experience has shown that when different microbial cultures are used with the same substrate (or substance to be transformed) varying results can be expected, and if the conditions for growth of the organisms vary from those reported as optimal, different transformations are likely to occur. For example, in one laboratory a strain of *Streptomyces fradiae* was used in the conversion of Reichstein's compound S to hydrocortisone (*42*) while in another laboratory the same strain grown under what were apparently slightly different conditions produced *epi*-hydrocortisone instead of hydrocortisone (*43*). The addition to the growth medium (intentionally or unintentionally) of traces of metallic ions such as zinc will lead to the formation of different metabolic products from progesterone by the mold, *Aspergillus ochraceus* (*44*). Another difficulty encountered is that the desired transformation product is often converted to other products if the incubation period with the microbial cells is extended. This may result in the accumulation of undesired products which make isolation of the prized material more difficult and lower the yield of the desired product (*45*). All of these factors should be considered in planning programs utilizing microbial processes for the transformation of organic substances and the carrying out of certain reactions. In addition to the knowledge of microbial techniques, some acquaintance with the analytical chemistry of organic compounds is helpful in determining quickly the extent of transformation so that highest conversion rates of added material to desired product can be secured. Filter paper partition chromatography and the techniques using liquid-liquid counter current separations have been especially useful in studying the transformations of steroids (*41*).

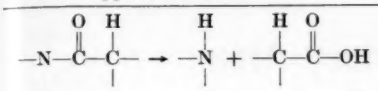
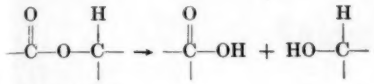
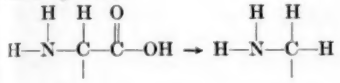
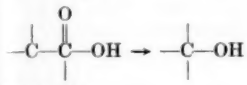
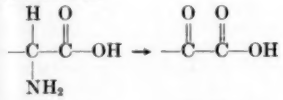
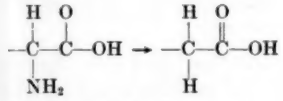
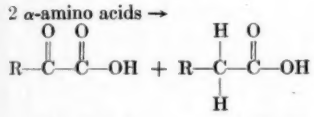
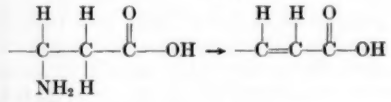
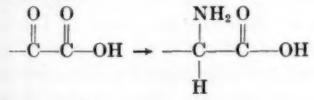
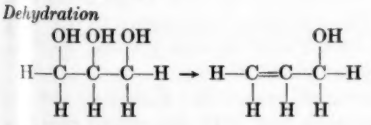
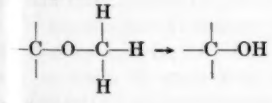
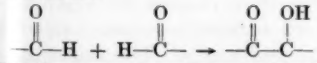
The examples listed in Table 1 represent only a few in the literature. Stodola (*1*) mentions that he has found more than 1400 examples of the use of microbial systems to carry out transformation of organic compounds. Microbial modification of such substances as alkaloids (nicotine, yohimbine, and reserpine), vitamins (nicotinic acid, pyridoxine, the cobalamins, and thiamin) and cancer antagonists (substituted purines) has led to the isolation of new and potentially useful chemotherapeutic agents as well as to a better understanding of the relationship of chemical structure and biological activity. It is evident that by utilizing microbial systems to carry out reactions the chemist has added another weapon to the arsenal at his disposal.

Literature Cited

(1) Stodola, F. H., "Chemical Transformations by Microorganisms," John Wiley & Sons, Inc., New York, 1958.
(2) Gale, E. F., "The Chemical Activities of Bacteria," 3rd ed., University Tutorial Press, Ltd., 1952.
(3) Oginsky, E. L., and Umbreit, W. W., "An Introduction to Bacterial Physiology," W. H. Freeman & Co., San Francisco, 1954.
(4) Perlman, D., Abstracts of 119th ACS Meeting, April, 1951, p. 24A.
(5) Moyer, A. J., et al., *Ind. Eng. Chem.*, **29**, 777 (1937).
(6) Wells, P. A., et al., *Ind. Eng. Chem.*, **29**, 1385 (1937).
(7) Shull, G. M., and Kita, D. A., *J. Am. Chem. Soc.*, **77**, 763 (1955).
(8) Meister, P. D., et al., *J. Am. Chem. Soc.*, **76**, 4050 (1954).
(9) Meystre, C., et al., *Helv. Chim. Acta*, **37**, 1548 (1954).
(10) Vischer, E., et al., *Helv. Chim. Acta*, **38**, 1502 (1955).
(11) Mann, K. G., et al., *Appl. Microbiol.*, **3**, 14 (1955).
(12) Bloom, B. M., and Shull, G. M., *J. Am. Chem. Soc.*, **77**, 5767 (1955).
(13) Fried, J., et al., *J. Am. Chem. Soc.*, **75**, 5764 (1953).
(14) Bruyn, J., *Koninkl. Nederl. Akad. Van Wetenschappen* **57** (*c*), 41 (1954).
(15) Harary, I., *J. Biol. Chem.*, **227**, 823 (1957).
(16) Fischer, F. G., and Wiedemann, O., *Ann.*, **513**, 260 (1934).
(17) Neuberg, C., and Welde, E., *Biochem. Z.*, **62**, 477 (1914).
(18) Farber, E., and Nord, F. F., *Biochem. Z.*, **112**, 313 (1920).
(19) Rothrock, J. W., et al., *Arch. Biochem. Biophys.*, **57**, 151 (1955).
(20) Abraham, E. P., and Chain, E. B., *Nature*, **146**, 837 (1940).
(21) Imaizumi, M., *J. Biochem. (Japan)*, **27**, 227 (1938).
(22) Casida, L. E., U.S. Patent 2,771,396 (1956).
(23) Sloane, N. H., et al., *J. Biol. Chem.*, **193**, 453 (1951).
(24) Horowitz, N. H., *J. Biol. Chem.*, **154**, 1415 (1944).
(25) Gale, E. F., *Biochem. J.*, **32**, 1583 (1938).
(26) Stickland, L. H., *Biochem. J.*, **28**, 1746 (1934).
(27) Quastel, J. H., and Woolf, B., *Biochem. J.*, **20**, 545 (1926).
(28) Otsuka, S. I., et al., *J. Gen. Appl. Microbiol.*, **3**, 35 (1957).
(29) Smythe, C. V., and Robb, L. A., U.S. Patent 2,606,899 (1952).
(30) Tachibana, S., et al., Int. Sym. on Enzyme Chem. (Tokyo), paper 116 (1957).
(31) Williams, W. J., and Thorne, C. B., *J. Biol. Chem.*, **210**, 203 (1954).
(32) Meister, A., *Adv. in Enzymology*, **16**, 185 (1955).
(33) Cardini, C. E., and Leloir, L. F., *Arch. Biochem. Biophys.*, **45**, 55 (1953).
(34) Huang, H. T., et al., *J. Am. Chem. Soc.*, **80**, 1006 (1958).
(35) Katagiri, H., and Kitahara, K., *Biochem. J.*, **31**, 909 (1937).
(36) Smiley, K., and Sobolov, M., *Bact. Proc.*, **14** (1958).
(37) Henderson, M. E. K., *J. Gen. Microbiol.*, **16**, 686 (1957).
(38) Neuberg, C., and Hirsch, J., *Biochem. Z.*, **115**, 282 (1921).
(39) Neuberg, C., and Mandl, I., *Enzymologia*, **14**, 128 (1951). U.S. Patent 2,511,867 (1950).
(40) Vischer, E., et al., *Experientia*, **12**, 50 (1956).
(41) Eppstein, S. H., et al., *Vitamins and Hormones*, **14**, 259 (1956).
(42) Colingsworth, D. R., et al., *J. Am. Chem. Soc.*, **74**, 2381 (1952).
(43) Fried, J., et al., *Recent Progr. Hormone Res.*, **11**, 157 (1955).
(44) Dulaney, E. L., et al., *Mycologia*, **67**, 464 (1955).
(45) Petersop, G. E., et al., *J. Bact.*, **74**, 684 (1957).

Table 1. Some Types of Modification of Organic Compounds by Microorganisms

Type of transformation	Example	Reference
Oxidations		
	Phenethanol to phenacetaldehyde	(4)
	Glucose to gluconic acid[a]	(5)
	Sorbitol to sorbose[a]	(6)
	Reichstein's compound S to hydrocortisone[a]	(7)
	Corticosterone to hydrocortisone	(8)
	Progesterone to deoxycorticosterone	(9)
	Hydrocortisone to prednisolone[a]	(10)
	Reichstein's compound S to cortisone	(11)
	$\Delta^{9(11)}$-Reichstein's compound S to 9β,11β-epoxy-compound S	(12)
	Testosterone to testololactone	(13)
	Hexadecane-1 to *l* (−) 1,2-hexadecanediol	(14)
	Nicotinic acid to 6-hydroxynicotinic acid	(15)
Reductions		
	Cinnamyl alcohol to hydrocinnamyl alcohol	(16)
	Benzaldehyde to benzylalcohol	(17)
	Acetol to optically active propylene glycol	(18)
Hydrolysis		
	Dioscorea saponins to diosgenin[a]	(19)

Type of transformation	Example	Reference
	Penicillin to penicilloic acid[a]	(20)
	Sterol ester to free sterol	(21)
Decarboxylations		
	Diaminopimelic acid to lysine[a]	(22)
	*p*-Aminobenzoic acid to *p*-aminophenol	(23)
Deaminations		
	α-Amino acids to α-keto acids	(24)
	Aspartid acid to succinic acid	(25)
2 α-amino acids → 	Glycine plus alanine to pyruvic acid plus propionic acid	(26)
	Aspartic acid to fumaric acid	(27)
Amination		
	α-Ketoglutaric acid to glutamic acid[a]	(28)
Phosphorylation		
sugar → sugar phosphate	Adenosine to adenosinetriphosphate	(29)
Transfer reactions		
transglycosylation	Riboflavin to riboflavinglucosides	(30)
transpeptidation	Glutamine to glutamylglutamic acid	(31)
transamination	α-Ketoglutaric acid plus alanine to glutamic acid plus pyruvic acid	(32)
transphosphorylation	Galactosamine plus adenosine-triphosphate to galactosamine-1-phosphate and adenosinedephosphate	(33)
Racemizations		
α-amino acids	Lysine[a]	(34)
α-hydroxy acids	Lactic acid[a]	(35)
Dehydration		
	Glycerol to acrolein[a]	(36)
Demethylation		
	*p*-Methoxybenzoic acid to *p*-hydroxy benzoic acid	(37)
Condensation		
	Benzaldehyde plus acetaldehyde to phenylacetylcarbinol[a]	(38)

[a] Carried out on an industrial scale.

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The Nineteenth Century Atom: Undivided or Indivisible?

The impression might be gained from both contemporary and older texts that the atom of the nineteenth century chemist was the smallest indivisible particle of an element. In his "Sourcebook on Atomic Energy," Glasstone (*5a*) writes, "During the nineteenth century most scientists would probably have regarded atoms as rigid spheres which were strictly indivisible, and consequently devoid of any internal structure." Ninety years previously, in his "Principles and Applications of Chemistry," the text used by the present author's grandfather while a student at Williston Academy, David A. Wells (*21*) wrote, "All matter is supposed to be composed of exceedingly small particles, which cannot be subdivided, or separated into parts. Such ultimate particles are termed atoms."

However, not all writers are so decisive in their statements. Muir (*12c*) does not give in 1884 an outright definition starting "An atom is. . .," but states, "The maximum atomic weight of an element is the smallest quantity, in terms of hydrogen as unity, of that element in the molecule of any compound thereof." And Roscoe and Schorlemmer (*14*) define an atom as "the smallest portion of matter which can enter into a chemical compound." The notable aspect of these definitions is that they are noncommittal as to the possibility of an atom's having an internal structure. Muir (*12a*) states that Dalton's use of the word atom for the smallest particle of both elements and compounds indicates that he did not regard his atoms as absolutely indivisible. This practice which seems odd to a modern reader was lauded by Williamson (*22*) in 1869 in his speech before the Chemical Society.

> It was a great step to extend the use of the word atom to groups of elements known to hold together only under certain limited conditions. For by including in one common term, atom, the smallest particles of the elements, and the smallest particles of these compounds . . . we deprive the word atom of the only objectionable peculiarity of which it can be accused. It is no longer an absolute term, and by its application to the elements it denotes the fact that they do not undergo decomposition under any conditions known to us. If anybody uses the word in its absolute sense in its present applications he is guilty of manifest inconsistency.

This presents the concept of the elementary atom as being the undivided in the then-known chemical processes and not as being indivisible by other as yet unknown methods or by mental procedures if not by practice. What were the reasons for this cautious attitude? Did the chemists of the nineteenth century have reasons for believing atoms of the elements to be compound? Yes, although the evidence was perhaps not conclusive, it was strong, and is worth considering.

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Belief in a Primary Matter

The first and fundamental reason for believing elementary atoms to be compound is not really a body of evidence at all. It was as Mendeleev (*10a*) called it in his 1889 Faraday Lecture a prejudice. He said,

> The periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old, but remarkably long-lived hope—that of discovering, if not by experiment, at least, by a mental effort, the *primary matter* . . . the idea has rendered good service . . . through awakened attempts either to confirm or to refute the ideas of Prout. . . . But again the idea could not stand the ordeal of experimental test, yet the prejudice remains and has not yet been uprooted.

This rather unfavorable statement, however, does not contain any flat statement that atoms have no internal structure. The argument is rather that one has difficulty in explaining how differences in elements arise if there is only one sort of primary matter and that both hydrogen and helium (which had been observed only in the sun) could hardly be it even if there was one.

Part of the impulse behind the belief in a primary matter was the feeling that there were too many elements. Thomas S. Kuhn (*7*) states that Boyle never really believed the definition of an element that he gives. In Boyle's mind, the apparent elements were differing arrangements of differing numbers of fundamental particles. So Boyle did not deny the possibility of transmutation and in fact attempted to accomplish one without any chemical agency. Boyle would have been happy if he had had the tools to observe radioactive changes and isomeric nuclear transformations. Gregory (*6a*) quotes Macquer as writing in 1766 that "*we* (his contemporaries) cannot divide atoms," implying that later workers may. He also states that Davy (*6c*) was disturbed by the number of elements in 1812. In fact, it appears that Davy proposed that some if not all elements contained hydrogen, and Priestley's friend Mitchell (*17*) in this country proposed that all elements which burn with a flame contain phlogiston (i.e., hydrogen) and cited Davy's work as the authority. The previous promulgation of such ideas is probably why Prout did not present his concept as completely novel (*cf. 5c*).

Davy's assistant and successor, Faraday (*1a*), is quoted by Crookes as saying, "To discover a new element is a very fine thing, but if you could decompose an element and tell us what it is made of—that would be a discovery worth making," and "At present we feel impatient, and to wish for a new state of chemical elements. For a time the desire was to add to the metals, now we wish to diminish their number." This all reflects an attitude toward nature that insists that 20, 40, 60, 90 elements are too many. The foundations should be more simple. In contemporary physics one

meets a similar feeling in such articles as that of Snell (*18*) who lists 28 particles and says in his introduction, "Physicists are faced with a complicated state of affairs that makes for a sense of frustration. Their experience and instincts tell them that there *must* be some organization underlying the empirical situation, but they have not yet been able to put a finger on a comprehensive theory."

As is well known, this attitude was formally stated in Prout's hypothesis that hydrogen is the protyle—the basic stuff of the universe and that atomic weights should be integral. This suggestion of Prout in 1815–1816 led to a lot of very careful atomic weight determinations and to attempts to explain away the few elements for which the deviations from whole numbers were very bad. All the atomic weight determinations refused to give exact whole numbers and Stas (*1c*) in particular declared in 1860,

> We must consider Prout's law as pure illusion, and regard the undecomposable bodies of our globe as distinct entities having no simple relation by weight to one another. The uncontestable analogy of properties observed amongst certain elements must be sought in other causes than those originating in the ratio of their reacting masses.

Like Mendeleev's previously quoted rejection of Prout's hypothesis (or law), this does not flatly deny any possibility of an internal structure, but only insists that the properties do not vary solely with the changing mass of the atoms and that atomic weights are not integral.

However, atomic weights did hug whole numbers very closely. Mallet (*8*), in 1880, after redetermining the atomic weight of Al and getting 27.019, wrote,

> As suggested by Marignac and Dumas, anyone who will impartially look at the facts can hardly escape the feeling that there must be some reason for the frequent recurrence of atomic weights differing by so little from accordance with the numbers required by the supposed law.

He goes on to state that 10 out of the 18 elements whose atomic weights were most precisely known come within one tenth of a unit of being integral. Using a binomial formula, he calculated the probability as being 1 to 1097.8. R. J. Strutt (*19*), later Lord Rayleigh, recalculated in 1901 the probability using nine elements and a formula of Laplace's giving the probability that the sum of the deviations from integers of all nine should be so small and concluded,

> The chance of such (accidental) coincidence being the explanation is not more than 1 in 1000, so that, to use Laplace's mode of expression, we have stronger reasons for believing in the truth of some modification of Prout's law, than in many historical events which are universally accepted as unquestionable.

Proposed Modification of Prout's "Law"

What were some of the modifications of Prout's law which were proposed? It is interesting that one reads so little about the fact that fractional weights could arise from mixtures of atoms having different, but integral weights. Glasstone (*5c*) states that Crookes and Schützenberger in the 1880's had ideas anticipatory of our isotopes. As far as Schützenberger (*16*) is concerned, this may well be, but the brief notes of his papers in the Bulletin of the French Chemical Society do not clearly state so. He reported that the analyses of apparently pure substances did not always agree and that these deviations might be due to changing atomic weights. However, how the weights changed from one case to another was not stated in print. Butlerov (*2*), commenting on Schützenberger's report and adding some similar examples from his own work, also speaks of changing atomic weights. He wrote,

> Let us set aside the atomic theory of the physicists along with the idea of atoms as the final, absolutely indivisible particles, what then is the atomic weight to the chemist? It is in reality nothing more than a certain weighable quantity of matter carrying a certain quantity of chemical energy. But we well know that for other forms of energy the quantity is far from being determined by the mass of matter. . . . Why not then the same thing for chemical energy, at least within certain narrow limits?

Butlerov felt that the motion as well as the amount of matter was concerned in the phenomena of chemical binding. It would appear that if one did not set aside the idea of absolutely indivisible atoms, then Butlerov's and Schützenberger's results would imply that the chemical atom was made of a number of these ultimate particles, which number varied with the conditions of formation of the compound. Actually, their results are probably due to impure compounds and incomplete reactions.

As for Crookes the matter is clearer. He was working in the field of the rare earths and their spectroscopy. He was able to prepare varying samples of certain of these elements all of which gave the same spectrum. He had a feeling that one type of atom should have one spectral line and that these varying preparations of the element were like isomeric organic compounds which were converted in the spark to a mixture of all of them giving the same total spectrum. Traube (*3b* and *1b*) reviews these ideas favorably in the *Zentralblatt* of 1887 and refers to Crookes' belief in the protyle out of which all the elements were formed during the cooling of the various solar systems. Crookes (*3a*) himself in his presidential address to the Chemical Society in 1889 said,

> Further, a compound molecule may easily act as an element. Take the case of didymium, which is certainly a compound, whether the products of Auer's operation be final or not. Didymium has a definite atomic weight; it has well-defined salts, and has been subjected to the closest scrutiny by some of the ablest chemists in the world. . . . We need some criterion for an element which shall appeal to our reason more clearly than the old untrustworthy characteristic of having not as yet been decomposed. . . . It may be that whatever body gives only one absorption band is an element. . . . It becomes more and more probable that between the atom and the compound we have a gradation of molecules of different ranks, which, as we have seen, may pass for simple elementary bodies.

In this last sentence it would appear that Crookes is using the word atom for the ultimate particle from which the apparent atoms of elements were composed. Nernst (*3c*) was not impressed. Reporting one of Crookes' papers in the *Zentralblatt*, he concludes,

> The famous investigator's phantasy-rich excretions cannot be reported thoroughly. In any case, Science will not accept such an alteration of previous belief based on either his present or former arguments against which many rebuttals can be opposed.

One of the earliest modifications of Prout's hypothesis was that of Dumas (*4*) who showed that the atomic weights of several series of elements could be surprisingly well expressed as arithmetic series—an extension of the Doebereiner triad concept. He proposed that the basic protyle was of atomic weight $^1/_2$ or perhaps

1/4. He lists the following sets of atomic (equivalent) weights and their differences:

Li	7	Mg	12	O	8	F	19
	(16)		(8)		(8)		(16.5)
Na	23	Ca	20	S	16	Cl	35.5
	(16)		(3 × 8)		(3 × 8)		(16.5 + 28)
K	39	Sr	44	Se	40	Br	80
			(3 × 8)		(3 × 8)		(19 + 28)
		Ba	68	Te	64	I	127

This reminded him of the changing atomic (equivalent) weights of the alkyl radicals and he wrote,

> The conclusion which I reached, which is also favorable to the opinion which I have long taught, is that there seems to be a similarity in composition between the radicals of organic chemistry and the radicals of inorganic chemistry, the latter of which we call elements.

In the same year, 1858, Pettenkofer (*13*) comments on Dumas' paper by saying that he had been saying the same thing for eight years.

Another suggestion is that of Marignac (*1d*) who in an article discussing that in which Stas rejected Prout's hypothesis remarks,

> While preserving the fundamental principle of that law, that is to say, while adopting the hypothesis of the unity of matter [Note—this is the driving impulse behind all such ideas], could we not make for example the following supposition.... Could we not suppose that the cause (unknown but probably different from the physical and chemical agencies familiar to us) which has determined certain groupings of the atoms of the sole primordial matter so as to give rise to our chemical atoms, by impressing on each of these groups a special character and particular properties, should not at the same time have exercised an influence on the manner according to which these groups of primordial atoms would obey the law of universal attraction, in such wise that the weight of each group might not be exactly the sum of the weights of the primordial atoms composing it?

This in 1860, Shades of the Mass-Energy relationship! It is interesting how often one meets in science suggestions which were not immediately followed up since they did not fit into the mental concepts of the period or because the techniques of the time did not permit their investigation.

The Periodic Law and Atomic Divisibility

The opinion of Mendeleev about atomic divisibility has been of considerable interest to the present writer since it was a statement in his *Annalen* paper (*10b*) on the periodic law that pointed out that many considered atoms divisible. He wrote,

> The discovery of such relations (those of Dumas) led to the comparison of the members of the various groups with those of homologous series and further to the chemico-mechanical conclusion on the compound nature of atoms, which is held to be probable by most chemists.

This is good testimony as to general opinion, but after reading Mendeleev's Faraday lecture, one wonders if he belonged to the majority who believed or to the minority who did not. However, in the footnotes of his text (*10e*) he says,

> For us the atom is indivisible, not in the geometrical abstract sense, but only in a physical and chemical sense. It would be better to call atoms indivisible *individuals*. The Greek atom equals the Latin individual, both according to etymology and the original sense of the words, but in the course of time these two words have acquired a different meaning. The individual is mechanically and geometrically divisible, and only indivisible in a special sense.

and (*10c*)

> Atoms are the smallest quantities or *chemically indivisible masses* of elements forming the molecules of *elements* and *compounds*.

The concept of the elements as individuals was firmly fixed in Mendeleev's mind and perhaps explains his lack of sympathy with the protyle concept. He did not think that it would be easy to explain the production of differing elements from one single substance. Quoting again from his text (*10d*),

> Chemistry, I am convinced, must occupy a place in the natural sciences side by side with mechanics; for mechanics treats of matter as a system of ponderable points having scarcely any individuality.... For chemistry, matter is a world of life, with an infinite variety of individuality both in the elements and in their compounds.

It would appear that the subject was an open one to Mendeleev. Atoms might be compound, but probably were not all built of hydrogen, helium, or any other known substance. The relations exhibited by the periodic table demanded an explanation and suggested that they were due to an underlying structure, but there was no concrete evidence as yet of its nature. One cannot help but feel that he would not dogmatically reject a hypothesis as to atomic structure that (*a*) had some concrete evidence in its favor, (*b*) could explain the atomic weight regularities, and (*c*) would account for the recurrence of similar, but not identical, properties.

Lothar Meyer (*11*), who divided the Nobel Prize for the periodic table with Mendeleev, starts his *Annalen* paper with the following clear cut testimonial:

> That the until-now undecomposed chemical elements are absolutely undecomposable materials is for the present at least very improbable. It seems more probable, that the atoms of the elements are not the ultimate but only proximate parts of molecules both of the elements and of their compounds. Thus the molecules are particles of the first order, the atoms are a second order which are composed of particles of a third and higher order.

Evidence from Spectroscopy

The regularities of atomic weights both in terms of Prout's law and the periodic table supported the inborn belief in the simplicity of matter, but there were other concrete lines of evidence. A second to arise was the results of spectroscopy. It was hard to reconcile the idea of rigid spheres with the complexity of spectra. Crookes' idea that elements might be made of numerous isomeric atoms each with a single spectral line has already been mentioned. The atoms must have periods of vibration, which implies various parts to vibrate and varying forces binding these parts. In his article on spectroscopy in the ninth edition of the *Encyclopaedia Britannica*, Arthur Schuster (*15*), Professor of Applied Mathematics at Owens College of Manchester, wrote,

> The spectrum of a body is due to a periodic motion within the molecules. If we are justified in believing that the molecule of mercury vapour contains a single atom, it follows that the atoms are capable of vibration under the action of internal forces, for mercury vapour has a definite spectrum. We may consider, then, the spectrum to be determined in the first place by forces within the atom, but to be affected by forces which hold together the different atoms within the molecule.

In regard to the results of spectroscopy, it should be noted that they led a number of persons to abandon the

Democritan atoms—solid objects surrounded by vacuum. Helmholtz proposed and William Thompson, Lord Kelvin, developed a concept of atoms being vortices in the luminiferous ether. In the same ninth edition of the *Encyclopaedia Britannica,* Clerk Maxwell (*9*) spends most of his space in an account of atomism in developing the mathematics of this idea and Muir (*12b*) in his treatise on the principles of chemistry, dedicated to Lord Kelvin, says, "The theory of 'vortex atoms,' developed by Sir William Thompson from the original concept of Helmholtz, explains spectroscopic facts. . .better than any other which has been suggested, and he (*12e*) refers to J. J. Thompson's Adams Prize Essay saying, "The theory of vortex atoms promises to help towards a solution of the problem of affinity. The theory has been applied to chemical combinations by J. J. Thompson."

Not all chemists either then or now have command of the mathematics necessary to understand the beauties of mathematical physics and so vortex atoms had more lip service than actual use in chemical investigations. One can read quite a bit of chemical history with only an occasional encounter with the term and with practically no encounter with the concept being applied effectively to chemical problems. It is interesting to note, however, that not all the scientists of 1870–80 were Democritan atomists and there were some who claimed not to believe in atoms at all. Commenting on Williamson's paper previously quoted, W. H. Walenn, F.C.S.(*20*), wrote, "These very atoms. . .have only existence in the minds of atomists and not a real existence." He also defends the concept of unlimited divisibility of matter stating that if one keeps on dividing a crystalline material one will never reach a place where the parts are not shaped like the large crystal. Walenn may have been an extremist, but others also preferred to avoid the use of the word atom as being too hypothetical.

Optical Isomerism

A third and final line of evidence supporting the concept of atomic structure is specifically chemical. It was the study of the *cis-trans* isomers by Wislicenus. It would be possible to explain optical isomerism without the concept of directed valences—the two groupings might perpetuate themselves since there might not be enough space around the central atom for four groups to surround it in a planar form and still be attached. But *cis-trans* isomers cannot be explained without directed valences and these can only be explained by a concept of internal structure. Admittedly this was resisted. Muir says (*12d*),

> In the present state of knowledge it is inadvisable to hazard hypotheses as to the inner structure of atoms in order to explain chemical phenomena. Atoms may not be homogeneous, but at present they are the ultimate particles to be considered in chemical changes.

However, Wislicenus was convinced that fumaric and maleic acids must both be butenedioic acids and he (*23*) testified in 1888,

> I therefore consider it more probable that atoms are not point-like energy carriers, but rather spacial structures composed of atoms of more fundamental elements. Therefore it seems to me more feasible than any other assumption, that atoms are comparable to compound radicals, and that—just as it is true of the latter—the units of affinity are located in certain parts of the same whence their activity originates.

So one must conclude that the nineteenth century chemists were not thoroughly given over to the idea of atoms being hard round marbles with vacuum between them. Some avoided the word "atom" like the pest—it was too hypothetical. Others believed that vortices in the luminiferous ether would be able to explain phenomena. Others were able to cite the regularities of atomic weights, spectroscopic phenomena, and the necessity of admitting directed valences for their belief that atoms had a structure made up of simpler particles. As R. Angus Smith (*5d, 6b*) in his preface to Graham's works implied, atoms were to be thought of as those particles which were not divided in ordinary chemical reactions and not as those particles which were absolutely indivisible both in thought and practice.

Literature Cited

(1) *Alembic Club Reprint,* No. 20, Prout's Hypothesis. Alembic Club, Edinburgh, **1932**: (*a*) p. 17. (*b*) pp. 18–20. (*c*) p. 47. (*d*) pp. 57–8.
(2) Butlerov, M. A., *Bull. soc. chim. France,* **39,** 267 (1883).
(3) Crookes, W., (*a*) *J. Chem. Soc.*, **55,** 284 (1889); (*b*) *Chem. Zentr.* [3], **18,** 399–400 (1887); (*c*) *Chem. Zentr.* [3], **19,** 705 (1889).
(4) Dumas, J., *Ann.* **105,** 74–108 (1858).
(5) Glasstone, Samuel, "Sourcebook on Atomic Energy." D. Van Nostrand Co., Inc., New York, **1950**: (*a*) p. 85, (*b*) p. 13, (*c*) p. 188, (*d*) p. 85.
(6) Gregory, Joshua C., "A Short History of Atomism, from Democritus to Bohr," A. and C. Black, London, **1931**: (*a*) p. 89, (*b*) p. 135, (*c*) p. 141, (*d*) p. 159.
(7) Kuhn, T. S., *Isis,* **43,** 12 (1952).
(8) Mallet, J. W., *Phil. Trans.*, **17,** 1034–5 (1880).
(9) Maxwell, J. Clerk, Encyclopaedia Britannica, 9th ed., Charles Scribner's & Sons, New York, **1878**, Vol. III, article "Atom."
(10) Mendeleev, D. I., (*a*) *J. Chem. Soc.*, **55,** 643, (1889); (*b*) *Ann.*, Suppl. Vol. **8,** 138 (1872). "The Principles of Chemistry," P. F. Collier & Son, New York, **1901**; (*c*) Part I, p. 324; (*d*) p. x–xi; (*e*) Part I, p. 216.
(11) Meyer, Lothar, *Ann.*, Suppl. Vol. **7,** 354 (1870).
(12) Pattison, Muir, M. M., "A Treatise on the Principles of Chemistry," Cambridge University Press, **1884**: (*a*) p. 8, (*b*) p. 27, (*c*) p. 36, (*d*) p. 124, (*e*) p. 450.
(13) Pettenkofer, Max, *Ann.*, **105,** 187–202 (1858).
(14) Roscoe, H. E., and Schorlemmer, C., "Treatise on Chemistry," D. Appleton & Co., New York, **1888**, p. 71.
(15) Schuster, Arthur, "Encyclopaedia Britannica," 9th ed., **1887**, Vol. 22.
(16) Schützenberger, P., *Bull. soc. chim. France* **39,** 258–62 (1883), **40,** 513 (1883).
(17) Siegfried, Robert, *Isis,* **46,** 327–36 (1956).
(18) Snell, Arthur H., *Am. Scientist,* **45,** 44–56 (1957).
(19) Strutt, R. J., *Phil. Mag.*, **6,** 1, 311–14(1901). P. S. Laplace, Theorie analytique des probabilities, Oevres Completes de Laplace, Gauthier-Villars, Paris, **1886**. Vol. 7, p. 257–60.
(20) Walenn, W. H., *Phil. Mag.*, **4,** 39, 122–6 (1870).
(21) Wells, David A., Wells Principles and Applications of Chemistry, New York, Iveson, Phinney & Co., **1860**.
(22) Williamson, A. W., *J. Chem. Soc.*, [2], **7,** 328 (1869).
(23) Wislicenus, Johannes, *Ber.*, **21,** 584 (1888).

✦ ✦ ✦

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Fuel Cells

The major portion of the electric power produced in the world today is generated through some form of heat engine operated by the combustion of fossil fuels—coal, oil, or natural gas. A three-step conversion process is required: transformation of the chemical energy of the fuel into thermal energy by combustion, transformation of the thermal energy into mechanical work in a heat engine, and transformation of this work into electrical energy by means of a generator. The fact that fossil fuels are at present our most widely distributed and least expensive primary energy source is an outstanding advantage for such a conversion process. However, the over-all efficiency of conventional electric power generation is restricted by incomplete combustion, heat losses, and the inherent limitations of mechanical devices. Furthermore, even under ideal conditions, the thermodynamics of heat engines places a limitation on the attainable over-all efficiency of converting thermal energy into mechanical work. Nuclear power plants now being designed also are subject to this thermodynamic limitation, which arises because of the restriction on temperatures attainable in practice for heat source and heat sink of the engine.

The thermodynamic limitations and most of the efficiency losses in the other steps in electric power generation could be avoided if the chemical energy of the fuel were converted directly to electrical energy. The high operating efficiency of electrochemical cells is well known, and if such cells were constructed, effectively using fossil fuels in some form for the anode (oxidizing) reaction, a practical source of electrical energy might be provided independent of the steam cycle and its inherent limitations. Electrogenetic cells employing common fuels (fuels cells) or products readily derived from fossil fuels have been studied on a laboratory scale for a number of years (*1*, *2*) and recent advances in improvement of their performance suggests that serious attention be given to this source of electrical energy.

Fuel cells, operating at ambient temperatures and employing fuel gases, are capable of a fuel-use efficiency of 70 to 80% compared with an efficiency of about 35% for a steam power plant operating on coal. On the basis of fuel consumed, modern electrical genrating plants require from 0.7 to 0.8 pound of coal per kilowatt-hour of electricity while a fuel cell would theoretically require the equivalent of only 0.3 pound of coal per kilowatt-hour. Other advantages of fuel cells would be their high ratio of electrical energy per unit weight, their adaptability for both large or small-scale applications, and their long operating life and storage characteristics. The components of the cell other than the fuel, are not consumed in the electrode reactions, and thus the cell could be operated indefinitely if the fuel were continually supplied.

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Types of Fuel Cells

The fundamental principles of operation of a fuel cell are essentially the same as those in all galvanic cells. Basically, we are concerned with two half-cell reactions —one involving oxidation and releasing electrons, the other involving reduction and requiring electrons. The two half-cells are separated by an electrolyte barrier so that reaction can occur only by the migration of ions. Such an arrangement of two half-cells is shown in Figure 1, where the fuel oxidized is hydrogen and the material reduced is the oxygen of the air. In this case the

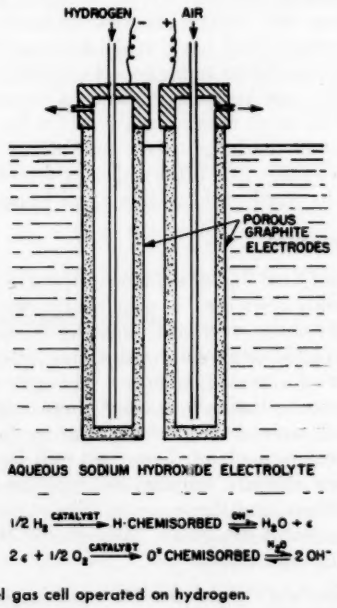
HYDROGEN
AIR
POROUS GRAPHITE ELECTRODES
AQUEOUS SODIUM HYDROXIDE ELECTROLYTE
1/2 H2 CATALYST H·CHEMISORBED OH⁻ H2O + ε
2ε + 1/2 O2 CATALYST O⁼ CHEMISORBED H2O 2 OH⁻

Figure 1. Fuel gas cell operated on hydrogen.

electrolyte is an aqueous solution of sodium hydoxide and the hydroxyl ions are the mobile species which serve to transport the oxidizing agent to the fuel electrode.

Carbon Cells. Since our fossil fuels are predominantly carbonaceous in nature, a cell in which carbon is used directly as the fuel electrode would appear advantageous. For example, in such a cell coal could be used as the anode where it would be oxidized to carbon dioxide in the half-cell reaction. Cells of this type have been constructed (*3*, *4*), and a schematic representation of such a cell is shown in Figure 2. In

this cell the half-cell reactions ideally[2] are:

$$C + 2O^{=}\text{-electrolyte} \rightleftharpoons CO_2 + \text{electrolyte}$$
$$4e^- + O_2 + \text{electrolyte} \rightleftharpoons 2O^{=}\text{-electrolyte}$$
$$C + O_2 \rightleftharpoons CO_2$$

Baur reports (*4*) that open circuit potentials of 0.83 volt can be obtained which under a current drain of 7 amperes per cubic foot of cell volume fall to 0.65 volt.

Unfortunately fuel cells utilizing carbon directly as the anode have several disadvantages. The oxidation

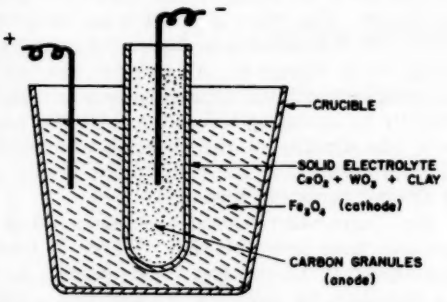

Figure 2. Direct carbon fuel cell after Baur (2).

of the carbon by the electrolyte species proceeds only at a negligible rate at room temperature. Thus, to obtain a reaction rate sufficient to permit reasonable current drain, the cell must be operated at high temperatures (around 800 to 1000°C). Operation of a fuel cell at temperatures greater than the temperature of its surroundings results in heat losses which represent a loss in efficiency. In addition, at temperatures where a high reaction rate is obtained, much of the fuel electrode would be consumed by carbon dioxide (the product of the electrode reaction) through the reaction:

$$C + CO_2 \rightleftharpoons 2CO$$

This represents an additional loss in efficiency of fuel utilization since the latter reaction does not contribute to the electrical energy of the cell. These limitations on the efficiency of cells directly employing solid carbonaceous fuels added to the difficulties encountered in high temperature operations make the direct carbon cell unattractive for commercial development.

Gas Cells. An alternative to the direct use of solid fuels is to use fuel gases—such as hydrogen or carbon monoxide—obtained either from the gasification of coal with steam or by the reforming of oil or natural gas. In a cell using a gas as fuel, oxidation of the gas must take place on the surface of a conductor since the gas itself cannot form a conducting electrode. Oxidation of fuel gases by the electrolyte species can usually be achieved at moderate temperatures by the use of proper catalysts, and in most cases no side reactions occur. Thus by employing fuel gases in a galvanic cell, the limitations imposed in the direct use of solid carbonaceous fuels are avoided. In the fuel gas cell shown in Figure 1, the gases, hydrogen and air, diffuse into the porous graphite electrodes which are impregnated with catalysts such as Fe-Co-Ni-group metals on the hydrogen side and Cu-Ag-Au-group oxides at the air electrode. The gases react with the electrolyte species on the surface of the catalysts according to the half-cell reactions shown. The graphite electrodes serve as conductors of the electrons flowing in the circuit, and a slight positive gas pressure prevents the electrolyte from flooding the electrodes. Several variations of fuel gas cells have been developed (*5*, *6*, *7*) employing both aqueous and molten salt electrolytes. Generally, alkali electrolytes are used in the hydrogen cells and carbonate electrolytes in those cells employing carbon monoxide.

A high pressure fuel gas cell which uses hydrogen as a fuel and which gives excellent current drain characteristics has been investigated by Bacon (*8*) at Cambridge University. This cell employs an aqueous hydroxide electrolyte and operates at a temperature of about 250°C with pressures up to 800 psi. The open circuit potential of the cell is 1.05 volts and current densities of 150 amperes per square foot of apparent electrode area at a potential of 0.9 volt can be developed. Although the Bacon cell represents one of the more promising cells being studied, there are still some obstacles to be overcome. As far as has been reported, no attempt has been made to use impure hydrogen as a fuel (for example, hydrogen obtained from the gasification of coal). The Patterson-Moos Division of the Universal Winding Company in the United States is currently engaged in the construction of fuel cell units of kilowatt size based on Bacon's original design. These cells employ porous nickel metal electrodes for the hydrogen half-cell reactions and lithium doped nickel oxide electrodes on the oxygen side. Power ratios of 60 watts per pound or 7 watts per cubic inch of cell volume are claimed.

A high temperature cell being investigated by the Pittsburgh Consolidation Coal Company by E. Gorin and H. L. Recht represents another approach to the development of fuel gas cells. This cell operates at temperatures of the order of 400 to 800°C using molten salts as electrolytes and such fuel gases as carbon monoxide and methane. Cells of this type offer one method for the direct use of light hydrocarbons. The hydrocarbons can be cracked directly in the cell to hydrogen and carbon and the carbon removed by including a small amount of carbon dioxide in the fuel gas stream. Reasonable current drain characteristics are obtained at the higher temperatures. Sintered iron electrodes are found to give good results when carbon monoxide is used as a fuel gas and lithium doped nickel oxide with a porosity of 30 to 40% and a mean pore size of 12 to 30 microns is used as the air (oxygen) electrode. The electrolyte, which generally is a carbonate eutectic, is contained in a porous magnesium oxide matrix.

Redox Cell. A third type of fuel cell has been proposed (*9*) which makes indirect use of the fuel as a reducing agent. An example of this type of cell, usually referred to as a redox cell, is illustrated in Figure 3. The electrolyte solutions, which are separated by a membrane impermeable to the active ions, contain ions that undergo oxidation and reduction in the cell. The electrolyte solutions are regenerated by using a carbonaceous fuel for reduction and air for oxidation. While there are no thermodynamic restrictions on the efficiency of this type of cell, in practice the regeneration of the electrolyte solutions offers many difficulties. Various metal ions in addition to the tin(IV) ion (used for illustration in Figure 3) can be reduced by coal in

[2] In practice carbon monoxide also is found to be a product of the electrode reaction.

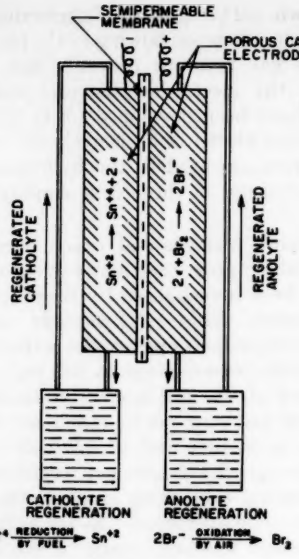

Figure 3. Redox fuel cell after Posner (7).

acid solution by autoclaving at moderate temperatures (circa 200°C). However, only a portion of the coal is active in the reduction which results in a very low fuel-use efficiency for the over-all process. The autoxidation of the bromide ion in acid solution by air proceeds satisfactorily when catalyzed by nitrogen dioxide.

Thermodynamics

Under thermodynamically reversible conditions the theoretical potential developed by a galvanic cell, $\mathcal{E}°$, is given by the equation,

$$-\Delta F° = n\mathfrak{F}\mathcal{E}°$$

where $\Delta F°$ is the difference in the free energy between the products and reactants in their standard states, n is the number of electrons involved in the cell reaction on a molecular basis, and $\mathfrak{F}$ is the Faraday Constant. The change in free energy, and hence the potential of the cell, can be determined at any other temperature if the enthalpy change for the reaction and heat capacities of the products and reactants are known. Since these data are commonly available, the theoretical potential of a cell can be calculated as a function of temperature for various fuels. In Figure 4 the results of such calculations are shown in a graph where the cell potential in volts is plotted against temperature. Typical reactions for the three types of cells described have been selected.

The potential expected from a single fuel cell is shown in Figure 4 to be of the order of one volt depending on the fuel oxidized and the temperature. Of course, higher voltages can be obtained by putting a number of cells in series. It is seen from Figure 4 that there is little to be gained thermodynamically by the use of high temperatures. Thus, if the electrode reactions had favorable rates at low temperatures and if diffusion were not a controlling factor, there would be no advantage in using high temperature cells based on considerations of the over-all reactions.

The influence of pressure on fuel cell potential can be calculated from the change in free energy of the cell reactions with pressure. The effect of pressure will be most pronounced in fuel gas cells where the reactants are both gases, and in this case can be expressed in the form:

$$\mathcal{E}_P = \mathcal{E}° + \Delta m \frac{RT}{n\mathfrak{F}} \ln P$$

for the conversion of gaseous reactants at pressure P into products in their standard states. In the above equation $\mathcal{E}_P$ is the cell potential at the pressure considered and Δm is the change in the number of moles in the gas phase. The effect of pressure on the potential of the fuel cell is illustrated in Figure 5 for the four reactions given in Figure 4. As was the case with increased temperature, little appears to be gained thermodynamically by operating fuel cells at higher pressures; however, the kinetics of the electrode reactions and diffusion processes are generally more favorable at higher temperatures and pressures.

So far only the over-all electrode reactions for fuel-cells have been discussed. There is, however, another aspect to the problem that appears to have been overlooked by previous investigators—that is, actual fuel cell electrode reactions do not necessarily correspond to the reversible over-all reactions from which theoretical potentials are calculated. For example, the oxidation of hydrogen in a reversible fuel cell would give a standard-state potential of 1.23 volts[3] at 25°C for the half-cell reactions:

$$\begin{array}{l} H_2 + 2OH^- \rightleftharpoons 2H_2O + 2e^- \\ {}^1/_2O_2 + H_2O + 2e^- \rightleftharpoons 2OH^- \\ \hline H_2 + {}^1/_2O_2 \rightleftharpoons H_2O \end{array}$$

[3] This value is based on liquid water at 25°C as the standard state for the product; however, in practice the product is in equilibrium with the aqueous hydroxide electrolyte and the actual potential is greater than 1.23 volts. Under current drain a peroxide mechanism is operative and the above standard state potential does not apply.

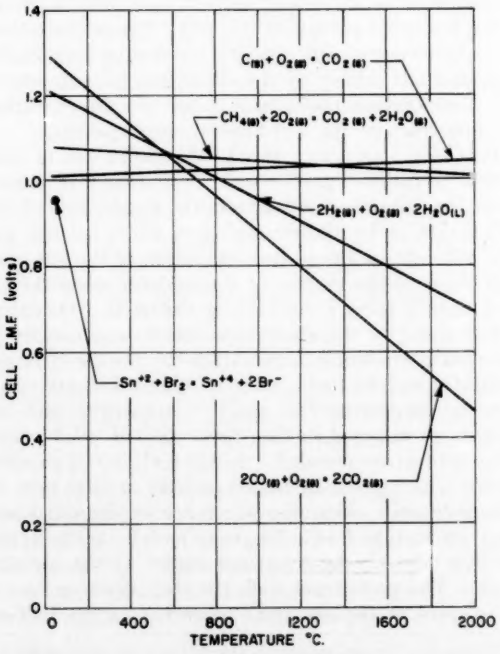

Figure 4. Temperature dependency of fuel cell reactions.

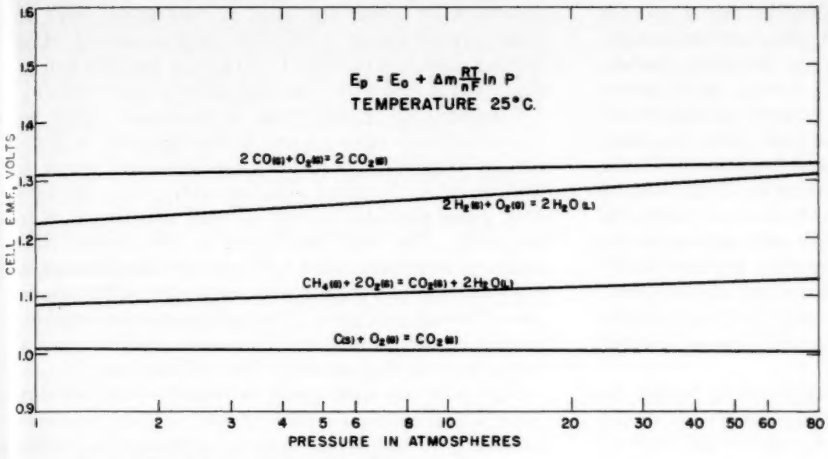

Figure 5. Pressure dependency of fuel cell reactions.

However, in an actual fuel cell the half-cell reactions cannot be expressed as simply as above since the gases (hydrogen and oxygen in the above illustration) are chemisorbed on the surface of the catalysts at their respective electrodes and should be represented as follows:

$$H_2 \longrightarrow 2H\text{-Chemisorbed} \overset{2OH^-}{\rightleftharpoons} 2H_2O + 2e^-$$

$$\tfrac{1}{2}O_2 + 2e^- \longrightarrow O^{=}\text{-Chemisorbed} \overset{H_2O}{\rightleftharpoons} 2OH^-$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

These latter equations imply that the equilibrium reaction which determines the potential of the cell is actually the equilibrium between the chemisorbed gases and the electrolyte and not between the free gases and the electrolyte. The chemisorption of the reactant gases is not a reversible process for the purpose considered here in that the heat of chemisorption is dissipated before reaction occurs, thus the greater the magnitude of the heat of chemisorption, the further the cell potential will be from that expected theoretically. This point is illustrated further in Figure 6 where the course of the reaction at the hydrogen electrode is represented. The open circuit (equilibrium conditions) potential of the cell would be expected to remain constant regardless of the catalyst employed if the free energy change corresponded to the over-all reaction. This is found not to be the case, but rather the cell potential varies directly with the heat of chemisorption of hydrogen on the catalyst. This means that since the open circuit potential is governed by the energy state of the chemisorbed hydrogen, the equilibrium reaction must be between the chemisorbed hydrogen and the electrolyte. Thus, the fuel cell electrode catalyst serves a dual purpose—it can enhance the open circuit potential of the cell as well as the kinetics of the cell reactions.

An example of the use of catalysts shows their enormous influence on fuel cell characteristics. If the fuel cell illustrated in Figure 1 is operated with only the porous graphite electrodes, an open circuit potential of about 0.1 volt is developed, and the potential rapidly falls to an immeasurably low value under current drain. When the porous graphite electrode on the hydrogen side of the cell is impregnated with palladium (extremely small amounts are adequate), the open circuit potential increases to about 0.8 volt. The potential at a current density of three amperes per square foot of actual electrode area is about 0.6 volt (the actual surface area of an electrode may be several times the apparent or geometric area, hence this value may correspond to 30 or more amperes per square foot of geometric area). Now, if in addition the electrode on the oxygen side of the cell is impregnated with silver-silver oxide, the open circuit potential increases further to 1.15 volts, a value close to the theoretical value of 1.23 volts, and the potential under current drain is again greatly enhanced.

Applications and Fuel Sources

Of the three general types of fuel cells described (direct carbon cells, fuel gas cells, and redox cells), the fuel gas cell is the only one presently being considered for commercial development. Fuel gas cells, while offering several distinct advantages over other types of fuel cells, suffer the limitation that at present only hydrogen and carbon monoxide can be used effectively as fuel sources (cells claiming to use hydrocarbons

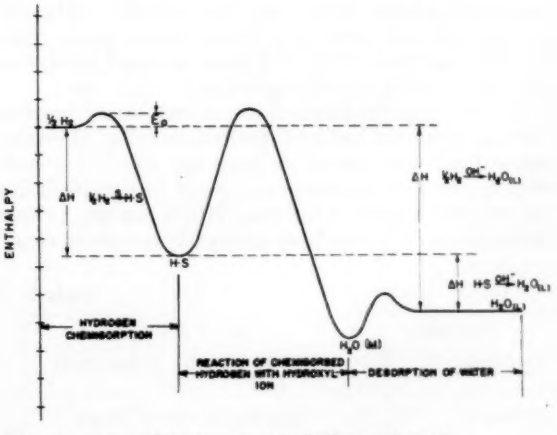

Figure 6. Course of the reaction at the hydrogen electrode.

generally depend on cracking of the hydrocarbon to produce hydrogen). Thus, the extent to which fuel cells will be used as large scale power sources in the near future will depend on the availability and cost of these gases as well as on progress made in further technological development of competing conventional and nuclear power sources.

In many small scale power applications, fuel cells can effectively compete with conventional storage batteries. The advantages offered by fuel cells are lower operating costs, the ability to be stored indefinitely, and long operating life. Such applications may include power sources for warehouse fork lifts and tractors,

mobile electronic devices, and stand-by power sources for hospital operating rooms and other service centers. A fuel gas cell manufactured by the National Carbon Company has been successfully tested as a power source for the Army's "Silent Sentry" mobile radar unit, and a small bank of these cells were operating lamps at the United States exhibit at the Brussels World Fair. In other applications requiring small amounts of electricity, such as railroad signal devices and telephone relay stations, fuel cells probably could furnish power more reliably and less expensively than present utility rates when maintenance and other costs are included. Thus, there would appear to be many practical applications and a ready market for small power output fuel cells.

The fuel gas for small scale applications would be hydrogen. Commercial tank hydrogen probably would be used in those cases where the storage weight ratio of compressed gases could be tolerated (ratio of weight of storage container to weight of fuel gas, which may be as large as 100 to 1 for compressed hydrogen). In those applications which require very low storage weight ratios, metal hydrides, lithium hydride in particular, would provide a convenient source of hydrogen. A little over eight grams of lithium hydride will yield about one cubic foot of hydrogen at STP, enough to produce over 50 watt-hours of electricity.

In order to realize the advantages of fuel cells for large scale electric power applications, the fuel costs for the cell should not greatly exceed those of fuels that would be used in the operation of conventional heat engines. Unfortunately, the cost of hydrogen or carbon monoxide per kilowatt-hour when used in a fuel cell is generally greater than the cost of the equivalent amount of coal used in a steam power plant, even though much less of the fuel gases are used because of the greater efficiency of the fuel cell.

Conventional gasification of coal has been suggested (*10*) as a source of fuel gases for fuel gas cells. However, present gasifiers cannot produce fuel gases at a sufficiently low cost to permit a fuel cell station operating on this fuel source to compete with a coal fired steam power plant. An improved gasifier design which would substantially lower the cost of fuel gases from this source would appear to offer the only possibility of converting coal into electrical energy via the fuel cell at a competitive cost with conventional power generation.

Underground gasification experiments have been conducted with some success in this country, in Russia, and in England. The fuel gases obtained are of low heating value, limiting their industrial use. However, such gases probably could be used effectively in fuel gas cells. The tests conducted in the United States indicate, at present, that underground gasification cannot successfully compete with the higher performance of conventional gasifiers. Thus, although not feasible at present, underground gasification of coal may in the future provide fuel gases for fuel cell stations.

Fuel cells can most easily provide low voltage direct current and would be ideal power sources for electrometallurgical industries such as an aluminium refining plant. An aluminium plant located in the southwest might find fuel gas cells operating on reformed natural gas an economical power source. The natural gas could be reformed with steam over a nickel catalyst to yield about 2700 cubic feet of hydrogen per thousand cubic feet of methane. Based on a cost for natural gas of \$0.20 per thousand feet at the well-head and including carbon dioxide removal from the reformed gas, a fuel cell station could produce electrical energy (5 volts dc at 1000 amperes) for a fuel cost of approximately four mills per kilowatt-hour.

Other potential fuel sources may be found in the oil industries refining plants, which produce considerable hydrogen in cracking and reforming operations, and in nuclear power plants. Water cooled nuclear reactors produce hydrogen and oxygen by the radiolysis of water—the amount depending on the operating conditions of the reactor. These gases might be separated by a diffusion process, taking advantage of the low molecular weight of hydrogen. Fuel cells, operated on the gases produced by radiolysis in nuclear power plants and stored during "off-hours," could provide a supplementary source of power during peak loads. Table 1 summarizes several fuel gas sources and comments on their applicability for various applications.

Table 1. Fuel Gas Sources

Fuel Gas	Source of fuel gas	Cell applications	Remarks
Hyd. gen	Metal hydrides, in particular lithium hydride	Missiles and portable electronic equipment	High fuel cost, favorable weight ratio *ca.* 4#/kw-hr for entire cell including liquid oxygen or peroxide storage
Hydrogen	Commercial tank hydrogen	Lift trucks and tractors, signal equipment, stand-by power sources	Moderate fuel cost, high weight ratio *ca.* 14#/kw-hr for entire cell including compressed oxygen storage
Hydrogen and carbon monoxide	Conventional gasification of coal	Large scale power sources	Impure gases (CO_2 and sulfur compounds), fuel cost using Koppers gasifier and oxygen *ca.* 9 mills/kw-hr
Hydrogen and carbon monoxide	Underground gasification of coal	Large scale power sources	Impure gases, less favorable economically in U.S. than conventional gasification
Hydrogen	Oil refineries (hydrogen produced in cracking and reforming operations)	Moderate sized power sources	Limited application because of restricted nature of fuel source, costs depend on other markets for this source of hydrogen
Hydrogen	Reforming of natural gas	Large scale power sources	Appears favorable in U.S. Southwest, fuel costs *ca.* 4 mills/kw-hr
Hydrogen	Electrolysis of water	Storage of electrical energy	Suggested as a method to relieve peak load problems, not of commercial interest at present
Hydrogen	Radiolysis and photolysis of water	Conversion of other energy forms into electrical energy	No information available

In summary, fuel cells should find many immediate applications as small power sources; however, the use of fuel cells for large scale power sources will depend on the economics of fuel gas supply, capital investment costs which are unknown at present, and future developments in fuel cells and competing nuclear and conventional electrical power plants. At present, large scale applications appear to be limited to those unique situations that require direct current in areas of high electrical costs but with low cost sources of fuel gases.

Literature Cited

(1) "Bibliography on Fuel Cells," British Electricity Authority, Kingston Road, Leatherhead, England, 1949.

(2) Howard, H. C., "Chemistry of Coal Utilization," (H. H., Lowry, *Editor*), John Wiley & Sons, Inc., New York, 1945, Vol. 2, Chap. 35.

(3) Baur, E., and Brunner, R., *Z. Electrochem.*, **43**, 725 (1937).

(4) Baur, E., and Preis, H., *Z. Electrochem.*, **43**, 727 (1937).

(5) Davttan, O. K., "Direct Conversion of Chemical Energy of Fuel into Electrical Energy," Academy of Sciences, Moscow, 1947.

(6) Bacon, F. T., *Beama J.*, **61**, 6 (1954).

(7) *Chem. Eng. News*, **35**, No. 38, 25 (1957).

(8) Bacon, F. T., British Patent 677,298 (1952).

(9) Posner, A. M., *Fuel*, **34**, 330 (1955).

(10) Gorin, E., U.S. Patents 2,570,543 and 2,581,650.

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Textbook Errors, 21

Weathering Reactions

Several textbooks[1] include in their discussion of weathering and clay formation an equation representing the process of chemical weathering of feldspar, usually written in the form:

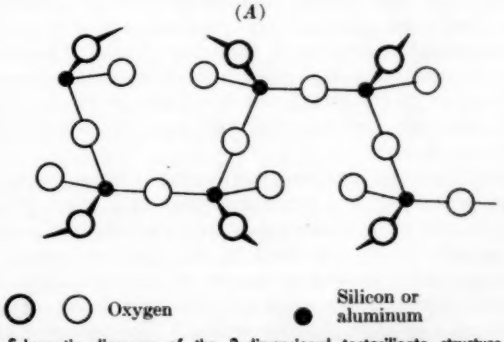
$$\underset{\text{Feldspar (orthoclase)}}{2KAlSi_3O_8} + 2H_2O + CO_2 = \underset{\text{Clay (kaolinite)}}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} + K_2CO_3 + \underset{\text{Sand (silica)}}{4SiO_2}$$

Often it is assumed that clay is merely the acidic residue after removal of bases and some silica from feldspar, and that no profound rearrangement of the feldspar structure is required. The released silica, it is sometimes stated, forms sand in the coarse fraction of the soil.

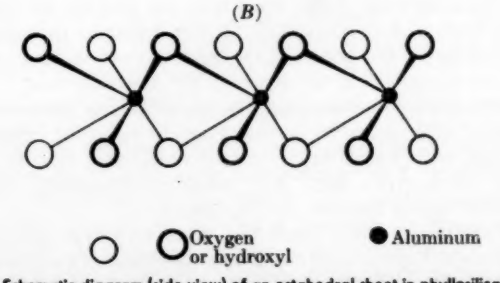
To the serious student of chemical weathering such statements or reactions sound obviously wrong, or at best a misrepresentation of the true facts. The weathering process is too complicated to be indicated by any one simple reaction. Hydrogen ions and not CO_2 are its main driving force, and neither K_2CO_3 nor sand are the products of weathering of feldspar.

The following discussion will outline briefly some pertinent points relating to weathering reactions, which can serve as background for a proper presentation of this subject. They pertain mainly to the initial formation of clays and do not deal with the vast and important subject of further weathering and transformation of these products.

Feldspars are tectosilicates (framework structures) with Al in 4 coordination; kaolinite and other clay minerals are phyllosilicates (layer structures) with Al in 6 coordination (see figure). Structurally there is no possibility that Al moves from its position of 4 coordination to that of 6 coordination merely by a slight



A. Schematic diagram of the 3-dimensional tectosilicate structure in feldspars. One fourth to one half of the 4 coordinated positions are occupied by aluminum, all others by silicon. The residual negative charge is balanced by alkali cations (not shown) which fit into cavities of the framework.



B. Schematic diagram (side view) of an octahedral sheet in phyllosilicates. The aluminum ions are 6 coordinated and there are adjacent parallel sheets (on top and below, not shown) of 4 coordinated silicon ions. The sheets are differently stacked to build the various clay minerals.

Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of errors discussed will not be cited. The error must occur in at least two independent standard books to be presented.

rearrangement of the lattice. In order that it may do so it must be released from the structure and all or practically all of its bonds must be broken. In the 6 coordination position the Al—O bond distance is increased by just over 10%, and this in fact is one of the characteristic crystallographic changes due to weathering.

A subject for discussion for a long time has been whether the decomposition of primary minerals proceeds until monomeric oxides and hydroxides in true solution are formed, or whether the decomposition produces polymeric colloidal aggregates. Most recent opinion favors complete decomposition except in special cases (*1*, *2*, *3*). The synthesis of the clay minerals presumably passes the colloidal stage, in either case, whether its building was begun from ions in solution or from groups of colloidal particles. What causes the reorganization of the randomly arranged skeletal groups into a layer structure is still unknown.

Mechanism of Weathering

On the basis of the information available today, chemical weathering can be visualized as follows. It is a typical solid state surface reaction. There must be first a chemical reaction at the surface of the solid with water, whereby the top layer becomes hydrated. This is greatly facilitated by broken and unsaturated bonds at the surfaces of the feldspar structure.

The decomposition reaction itself is mainly a hydrolysis and ion transfer (replacement) reaction, and at first affects only a few layers of ions at the surface. However, as the bonds become weakened, small clumps of ions detach themselves from the surface and the same process may continue and eventually decompose the interior of the mineral (*4*). The large cations are relatively easily mobilized and released. Subsequently the SiO^{-}_{4} and AlO^{-}_{4} groups of the feldspar structure are attacked and pass into solution as hydrous oxides.

Although the chemical weathering reaction requires only water for its implementation and takes place also in neutral or alkaline solutions, the rate of reaction is usually much enhanced in an acid environment. The necessary hydrogen ion can be supplied from the dissociation of water, from carbonic acid, from organic acids, or any other possible source. The nature of the accompanying anion as such is irrelevant in the process, although side reactions with the anion may be of significance in influencing the rate and direction of the over-all process.

The smallness of the hydrogen ion enables its easy penetration into "cracks" of the feldspar structure especially where bonds have been weakened, and one of its functions is to displace the metallic ions (*4*). These released cations may be absorbed by the newly formed clay in exchangeable form to saturate broken bonds and unsaturated valences of the structure, but more often they are removed eventually and leached out by the percolating water.

$CaCO_3$ or other insoluble salts may precipitate, but under slightly acid conditions and sufficient leaching it is highly unlikely that carbonates would precipitate in the immediate weathering environment. Where the precipitation and deposition of carbonates and soluble salts occurs, it is because the transported solution has encountered a different physicochemical environment. K_2CO_3 has never been reported as a product of weathering, and neither is it found in association with kaolinite.

Silica, when released by weathering, does at times polymerize and may form large sized aggregates of chalcedony or opal, but such secondary particles rarely form the bulk of sand. Ordinarily the sand fraction in soils is composed of quartz and other stable mineral particles originally present in rocks, which have proved resistant to the attack of weathering. If silica released from the feldspar does not participate in clay mineral synthesis, it is usually removed from the system in solution as undissociated H_4SiO_4 (*5*) or it may precipitate as more or less amorphous colloidal particles.

The behavior of released aluminum or iron oxides depends very much upon the prevailing environment. Under tropical conditions of strong leaching and where the *p*H is neutral to alkaline, the hydrous oxides remain largely separated upon deposition. Silica is preferentially leached from the system, leaving a residual product rich in hydrous aluminum and iron oxides called bauxite or laterite. Contrarily, in a strongly acid environment and in the presence of organic chelators from the residues of plants, aluminum and especially iron are preferentially leached and there may be a relative enrichment of silica. Under moderately acid conditions and leaching, however, the released aluminum and iron oxides will recombine with the released silica to form the layered clay minerals. Depending on the relative proportions of the hydrous oxides and on other ions present, a variety of clay minerals can be formed.

Thus weathering reactions in nature rarely proceed in chemically well-defined systems. Decomposition and synthesis are continuous processes without any sharp break, and both the starting materials and the end products are usually extremely heterogenous. Also, the schematic formulas used to represent clay and other complex minerals only approximate the true composition of the reactants. All this must always be borne in mind when stoichiometrically balanced reactions are written. In order to avoid problems of balance and associated products it is best to separate the decomposition reaction from the synthesis of the product, or at least to think of them as stages of one continuous process.

However, for didactic reasons, i.e., to lend assurance that the reactions occur in a simple describable way (*6*) and for various physicochemical calculations, it is sometimes desirable and convenient to have stoichiometrically balanced reactions.

Weathering of Feldspar Producing Kaolinite

In view of what has been said above, the weathering of K-feldspar to kaolinite is closely represented by the following reaction:

$$\underset{\text{Orthoclase}}{2KAlSi_3O_8} + \underset{\text{Water}}{11H_2O} \rightarrow \underset{\text{Intermediate products}}{(\text{cations and hydrous oxides})} \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{Soluble salts and ions}}{4H_4SiO_4 + 2K^+ + 2OH^-}$$

This reaction indicates that the weathering of silicate

minerals is essentially a hydrolysis reaction and the generally recognized fact that the weathering solution increases alkalinity.

If it is desired to stress the significant role of hydrogen ion in weathering rather than the increase in alkalinity, the reaction is best written:

$$\underset{\text{Orthoclase}}{2KAlSi_3O_8} + 2H^+ + 9H_2O \rightarrow \underset{\text{Intermediate products}}{(\text{cations and hydrous oxides})} \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H_4SiO_4 + 2K^+$$

Both reactions emphasize the relatively large amount of water required in weathering and that besides clay (kaolinite) other possible products are soluble salts and silica. This is in conformity with true and observed facts (*3*).

Reactions similar to those above can be written for the other minerals of the feldspar family, for instance:[2]

$$\underset{\text{Anorthite}}{CaAl_2Si_2O_8} + 2H^+ + H_2O \text{ —( )} \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + Ca^{++}$$

$$\underset{\text{Plagioclase, } Ab_{67}An_{33}}{2NaAlSi_3O_8 \cdot CaAl_2Si_2O_8} + 4H^+ + 10H_2O \text{ —( )} \rightarrow 2\underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H_4SiO_4 + 2Na^+ + Ca^{++}$$

In anorthite the Al/Si ratio is similar to that in kaolinite and no silica is therefore formed. With plagioclase as starting material the amount of silica and soluble salts obtained will depend on the exact composition of the mineral.

Hydrous Mica and Montmorillonite as Weathering Products

Besides minerals of the kaolinite group, both beidellite (Al-montmorillonite) and illite (hydrous mica) are possible products of weathering of pure feldspar. The presence of released cations is here of special significance in that they serve as exchangeable and interlayer ions.

Hydrous micas are obtained in the laboratory from K-feldspars under conditions of accelerated weathering (*7*), and have also been identified as an intermediate stage, between the decomposition of alkali feldspar and the formation of kaolinite (*8*). Schematically the reaction can be depicted as follows:

$$\underset{\text{Anorthoclase}}{3KAlSi_3O_8 \cdot 6NaAlSi_3O_8} + 6H^+ + 36H_2O \text{ —( )} \rightarrow \underset{\text{Hydrous mica}}{3KAl_2(Si_3Al)O_{10}(OH)_2} + 18H_4SiO_4 + 6Na^+$$

$$\underset{\text{Hydrous mica}}{2KAl_2(Si_3Al)O_{10}(OH)_2} + 2H^+ + 3H_2O \text{ —( )} \rightarrow \underset{\text{Kaolinite}}{3Al_2Si_2O_5(OH)_4} + 2K^+$$

If we represent montmorillonite schematically by $Al_2Si_4O_{10}(OH)_2 \cdot xH_2O$, disregarding lattice substitution and the exchangeable ions, we can write a weathering reaction producing montmorillonite as follows:

$$\underset{\text{Albite}}{2NaAlSiO_3} + 2H^+ + (x + 4)\,H_2O \text{ —( )} \rightarrow \underset{\text{Montmorillonite}}{Al_2Si_4O_{10}(OH)_2 \cdot xH_2O} + 2H_4SiO_4 + 2Na^+$$

With anorthite as starting material there would be an excess of aluminum oxide instead of silica. If we however take into account lattice substitution in the silica layer, we obtain

$$\underset{\text{Anorthite}}{3CaAl_2Si_2O_8} + 6H^+ + xH_2O \text{ —( )} \rightarrow \underset{\text{Beidellite}}{2Al_2(Si_3Al)O_{10}(OH)_2 \cdot xH_2O} + 3Ca^{++}$$

Reactions with plagioclase can be written in a similar way.

Montmorillonite has been successfully synthetized in the laboratory with albite as starting material (*7*, *9*), but the writer is aware of only one such observation from nature (*10*).

Though it is often considered that the montmorillonite group minerals form under environmental conditions which are different or antithetical from those under which kaolinite is formed (*6*), both minerals are found side by side in soils. To represent this reaction we may write, using plagioclase as starting material:

$$\underset{\text{Plagioclase, } Ab_{50}An_{50}}{2NaAlSi_3O_8 \cdot 2CaAl_2SiO_8} + 6H^+ + (x + 1)\,H_2O \text{ —( )} \rightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{Montmorillonite}}{2Al_2Si_4O_{10}(OH)_2 \cdot xH_2O} + 2Na^+ + 2Ca^{++}$$

More commonly, however, montmorillonite and other 2Si:Al layer clay minerals will require the presence of magnesium or iron for partial substitution of silicon and aluminum ions in their lattice structure, and cannot therefore be formed from pure feldspars.

Schematic weathering reactions similar to those above can be written for any other mineral as starting material, and have also been successfully applied to rocks of known composition (*11*), and to the pedosphere as a whole (*12*). Again, as in the examples above, the only substances added during weathering are hydrogen ions and water, and soluble salts and silica are removed.

In all these weathering reactions it is intrinsically understood that the primary minerals completely decompose and the elements rearrange in order that clay mineral structures can be formed. The only exception is in the case of mica (biotite and muscovite) as starting material. Due to its structural relationship to the 2Si:Al layer clay minerals, a sequence of new minerals *can* be formed by minor replacement of certain ions, mainly hydronium $(H_3O)^+$ for potassium and by a slight alteration of the lattice, accompanied by its expansion and the entry of water between the layers (*2*, *13*, *14*, *15*). However, whether these theoretical alterations of mica into expanding clay minerals really do take place in nature is still a matter of discussion.

Energetics and Kinetics of Weathering

Weathering processes are good examples of coupled reactions, in that both endothermic and exothermic reactions take part in its course. The over-all reaction, being a product of a number of simultaneous equilibria, is spontaneous and irreversible at temperatures prevailing at the earth's surface. Yet thermodynamic calculations indicate that the decrease in free energy may be relatively small. However, it can also be seen from the weathering reaction that the process is

[2] ( ) For the sake of brevity, the intermediate step will be designated by this sign, implying continuous decomposition followed by reconstitution of new mineral structures.

pushed to the right by repeated leachings with large amounts of fresh water since the soluble products are constantly removed and the system thereby kept at its initial reactive state. This is apparently what happens in nature. Given sufficient time, all feldspar and other minerals will decompose and serve as material for clay formation. The ultimate energy which drives the process is of course derived from the radiant energy of the sun.

The process of weathering is usually slow, but the rate can be enhanced by elevated temperatures. This is what has happened in extensive deposits of clays of geologic origin, in which the process has gone almost to completion. In such products usually one specific clay mineral dominates and by far outnumbers the remaining accessory minerals. In soils, on the other hand, all the stages of the weathering process are represented, including reactions of alteration and decomposition of the secondary clay minerals themselves (*16*, *17*). Superimposed on that are the biological processes of soil formation. Thus the mixture of clay minerals and residual minerals which is found in soils is extremely variable and heterogenic.

To summarize, it has been demonstrated that insufficient regard is given to the complex weathering reaction in depicting it by one stochiometrically balanced equation. The various aspects of the mechanism of weathering can perhaps be best discussed by presenting a generalized equation in the form:

aluminum silicate mineral + water → ions and amorphous intermediate products → clay + soluble salts

Where it is preferred to present balanced equations, their limitations should be acknowledged and several alternate possibilities of both end products and starting materials should be explored and discussed.

Acknowledgment

The writer is indebted to Professor Karol J. Mysels for helpful suggestions in improving the presentation of this paper.

Literature Cited

(1) Correns, C., and Engelhardt, D. von, *Chemie d. Erde*, 12, 1 (1939).
(2) Fieldes, M., and Swindale, L. D., *New Zealand J. Sci. Techn.*, **36B**, 140 (1954).
(3) Keller, W. D., "The Principles of Chemical Weathering," Lucas Bros, Columbia, Miss., **1957**.
(4) Frederickson, A. F., *Bull. Geol. Soc. Amer.*, **62**, 221 (1951).
(5) Krauskopf, K. B., *Geochim. Cosmochim. Acta*, **10**, 1 (1956).
(6) Keller, W. D., *Bull. Am. Assoc. Petrol. Geologists*, 40, 2689 (1956).
(7) Norton, F. H., *Am. Mineralogist*, **22**, 1 (1937); *ibid.*, 24, 1 (1939); *ibid.* **26**, 1 (1941).
(8) Sand, L. B., *Am. Mineralogist*, **41**, 28 (1956).
(9) Sand, L. B., Roy, R., and Osborn, E. F., *Econ. Geol.*, 52, 169 (1957).
(10) Neuwirth, E., *Carinthia II.*, **64**, 32 (1954).
(11) Keller, W. D., Kiersch, G. A., and Howell, P., *Proc. Third Natl. Conf. Clays and Clay Minerals. Natl. Res. Counc. Publ.* **395**, 413 (1955).
(12) Mattson, S., *Ann. Roy. Agr. Coll., Sweden*, **5**, 261 (1938); *Soil Sci.*, **51**, 407 (1941).
(13) Brown, G., and Norrish, K., *Mineral. Mag.*, **29**, 929 (1952).
(14) Mackenzie, R. S., *Potassium Symposium*, Intern. Potash Inst., Bern, **1955**, 123.
(15) Uchiyama, N., *Tohoku J. Agr. Res.*, **7**, 1 (1956).
(16) Jackson, M. L., et al., *J. Phys. & Colloid Chem.*, **52**, 1237 (1948).
(17) Jackson, M. L., and Sherman, D., "Advances in Agronomy," Academic Press, Inc., New York, **1953**, Vol. 5, p. 221.

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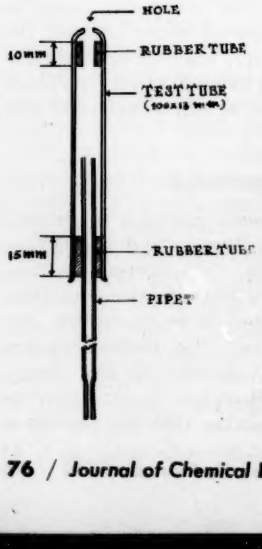
Device for Pipetting Pathogenic Organisms



With an ordinary Pyrex test tube (100 × 13 mm) and two short pieces (about 15 mm and 10 mm) of rubber tubing of suitable diameter to fit the test tube snugly and of bore size same as the outside diameter of pipet, a very simple suction device can be made for pipetting strong acids, alkalies, KCN solutions, and suspensions of pathogenic bacteria and fungi.

A small hole is conveniently made at the bottom of the test tube by first grinding a little with a flat file and then sharply hammering a pointed needle from inside after holding the test tube in upright position over a hole in a rubber cork.

With a little care the hole could be made quite uniform and could be conveniently closed by the forefinger as in an ordinary pipetting operation. The smaller piece of rubber tube is then pushed down to the bottom of the tube (to prevent pipet from hitting the bottom of the test tube) and the larger piece fitted at the mouth. The suction end of the pipet is introduced into the test tube through the rubber tube (see figure). By holding the pipet with the left hand and moving the test tube up with the right hand keeping the hole closed with forefinger, the liquid to be pipetted can be sucked in and delivered as usual. A little lubrication will greatly facilitate the movement of the test tube.

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Balancing Organic Redox Equations

Most methods of balancing redox equations are based on empirical formulas of the materials involved and complete electron transfer or its equivalent (change in oxidation number, half reactions, etc.). Few texts on organic chemistry present any pattern for solving such problems. Reluctance to do so may be due to the difficulty in demonstrating electron transfer in covalent compounds.

In teaching organic chemistry, emphasis is usually placed on structural rather than empirical formulas, in part to explain reaction mechanisms.

This paper presents a method based on the study of structural formulas and an artificial device—the use of hypothetical free radicals. Though the method is empirical, equations can be balanced by *inspection*. Better still, the student can visualize the steps involved.

Oxidations of organic compounds often involve the breaking of particular covalent bonds. Such bonds may easily be found by comparing the structure of each reactant and those of its products. For *convenience*, let us assume that the electrons in each ruptured bond are divided symmetrically to produce two free radicals. Each of these will require another radical, usually from the oxidizing agent, to yield a whole molecule.

Consider the oxidation of an aldehyde to an acid by hydrogen peroxide. First imagine the dissociation of H_2O_2 to produce two free hydroxyl radicals.

$$H—O—O—H \rightarrow 2\cdot O—H$$

To emphasize its single unpaired electron, the radical will be written as $\cdot OH$, which will be the effective oxidant in subsequent reactions.

The usual expression

$$RCHO + H_2O_2 \rightarrow RCOOH + H_2O$$

may be rearranged slightly for clarity.

$$\begin{array}{l} HO\cdot\ \cdot OH \rightarrow HO \\ RC:H \qquad\quad R\ddot{C} \\ \quad\| \qquad\qquad\ \| \\ \quad O \qquad\qquad\ O \end{array} \quad \begin{array}{l} \\ | \\ \\ \end{array} \begin{array}{l} OH \\ \ddot{H} \\ \\ \end{array}$$

One covalent bond in the aldehyde has been broken by two free radicals. Also, the total oxidation number of the oxygen atoms changes from -2 to -4. These observations lead to two general rules, to be substantiated later:

(1) *The net change in oxidation number of the inorganic oxidizing agent is equal to the number of usable radicals produced.*

(2) *Usually, two free radicals are required for the rupture of each (single) covalent bond.*

Occasionally, however, a covalent bond can be ruptured by a single free radical if a matching *organic* free radical is produced as intermediate. The oxidation of a mercaptan to a disulfide illustrates this point. The reaction is usually expressed:

$$2RS—H \xrightarrow{(O)} RS—SR$$

Since two S-H bonds must be broken, two free radicals from a suitable source will combine with the two hydrogens. The two RS $\cdot$ radicals are free to combine.

Oxidizing agents may require water or various other materials in order to produce the requisite free radicals.

	Change in oxidation number
$KMnO_4$ (dil, alkaline) $+ 2H_2O \rightarrow KOH + MnO_2 + 3\cdot OH$	(Mn: $7 \rightarrow 4$)
$KMnO_4 + 2H_2SO_4$ (excess) $\rightarrow KHSO_4 + MnSO_4 + 5\cdot OH$	(Mn: $7 \rightarrow 2$)
$K_2Cr_2O_7 + 5H_2SO_4 \rightarrow 2KHSO_4 + Cr_2(SO_4)_3 + 6\cdot OH$	2(Cr: $6 \rightarrow 3$)
$HNO_3 + H_2O \rightarrow NO + 3\cdot OH$	(N: $5 \rightarrow 2$)

A perfect material balance has been attained without the use of ionic forms. In each case, the number of free radicals produced is equal to the change in oxidation number. This applies to all inorganic oxidants studied to date.

Although the use of free radicals for all oxidation reactions does require a hypothetical assumption, it requires no more than other empirical methods. And, of course, in some reactions free radicals are known to be at work, e.g., vapor phase nitration or chlorination of paraffins. These are but special cases of oxidation. They can be balanced in just the same way as the oxidation of the aldehyde.

Example: The Oxidation of Propylene

$$CH_3—CH=CH_2 + KMnO_4 \rightarrow CH_3COOH + H_2CO_3 + KOH + MnO_2 \pm (?)\ H_2O$$

On comparing the structure of propylene with those of acetic acid and carbonic acid, one will observe that a total of five bonds have to be ruptured. These will require ten free hydroxyl radicals.

$$CH_3—\overset{H}{\underset{|}{C}}{}^{1}=\overset{H}{\underset{|}{C}}{}^{2} — H \rightarrow CH_3—\overset{OH}{\underset{OH}{C}}—OH + HO—\overset{OH}{\underset{OH}{C}}—OH + HOH$$

Each hydrated form of the acids (acetic and carbonic) accounts for one more molecule of water. Obviously, the gain or loss of water has nothing to do with a redox system. The same applies to the subsequent neutralization of the KOH generated.

Since each $KMnO_4$ offers three radicals, a total of 30 radicals will be necessary for three molecules of propylene.

$$3CH_3—CH=CH_2 + 10KMnO_4 + 20H_2O \rightarrow 3CH_3COOH + 3H_2CO_3 + 10KOH + 10MnO_2 + 15H_2O$$

The final reaction, after neutralization, is

$$3CH_3CH{=}CH_2 + 10KMnO_4 \rightarrow 3CH_3COOK + 3K_2CO_3 + 10MnO_2 + KOH + 4H_2O$$

Further observation leads to two additional rules that are valid only in the use of *hydroxyl* radicals.

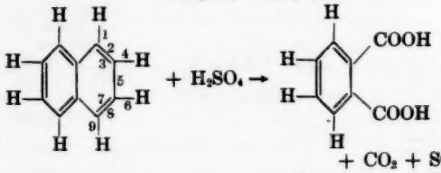
(3) *Each C—H bond broken produces one molecule of water.*

(4) *Each double bond between carbon atoms yields two molecules of water, resulting from the usual dehydration of a molecule having two hydroxyl groups on a common carbon atom.*

Example: The Oxidation of Naphthalene

The preparation of phthalic acid by the oxidation of naphthalene via sulfuric acid in the presence of a mercuric salt may seem to be a massive problem, yet it can be visualized readily. Since the oxidation number of sulfur changes from six to four, *two* free radicals are produced per molecule.

$$H_2SO_4 \rightarrow SO_2 + 2\cdot OH$$



$$+ CO_2 + SO_2 \pm (?)\ H_2O$$

Comparison of the extended structures of naphthalene and phthalic acid shows that nine covalent bonds are ruptured. Therefore, 18 free radicals are required. Thus we can write:

$$C_{10}H_8 + 9H_2SO_4 \rightarrow C_6H_4(COOH)_2 + 2H_2CO_3 + 9SO_2 + 8H_2O$$

Because carbonic acid is unstable in such a system, $2CO_2$ and two additional molecules of water would be in the final equation.

Formation of Coordinate Bonds

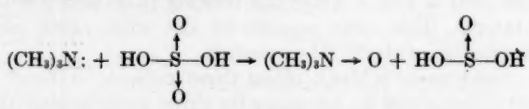
The preparation of an amine oxide from the corresponding amine results in the formation of a coordinate covalent bond, rather than the rupture of a simple covalent bond. This is often illustrated by the use of hydrogen peroxide.

$$(CH_3)_3N + H_2O_2 \rightarrow (CH_3)_3N \rightarrow O + H_2O$$

The equation is balanced as shown, but the use of two hydroxyl radicals illustrates a new principle for the present study.

$$(CH_3)_3N{:} + 2\cdot OH \rightarrow (CH_3)_3N\langle^{OH}_{OH} \rightarrow (CH_3)_3N \rightarrow O + H_2O$$

If sulfuric acid were suitable for such a conversion, one would see the effective transfer of a semipolar bond from one molecule to another.



At this point, another rule is in order:

(5) *Two radicals are required to form a new coordinate covalent bond.*

In solving problems involving complex ions (as cyanides) it it convenient to imagine each ion hydrolyzing to form neutral molecules. Again, the addition or loss of water is legitimate since this has no effect on a redox system. Consider

$$K_4Fe(CN)_6 + H_2SO_4 + KMnO_4 \rightarrow KHSO_4 + Fe_2(SO_4)_3 + MnSO_4 + HNO_3 + CO_2 + H_2O$$

The first step is to convert (hydrolyze) $K_4Fe(CN)_6$ to 4KOH, $Fe(OH)_2$, and 6H-C≡N. The oxidation products would be

$$Fe(OH)_3,\ H_2O,\ CO_2 \text{ and } HO\overset{\overset{O}{\|}}{N} \rightarrow O.$$

Therefore, one radical would take care of the oxidation of the iron. The four covalent bonds in HCN would require eight radicals, and the formation of the coordinate bond in HNO_3, two more. Thus $1 + 6(8 + 2)$ indicates that 61 radicals would be needed to oxidize the entire molecule. Since the manganese undergoes a change of five units in oxidation number, the ratio of $K_4Fe(CN)_6$ to $KMnO_4$ must be 5:61. Five atoms of iron would make a discrepancy in $Fe_2(SO_4)_3$, the ratio of 10:122 is more suitable. From that point, the number of molecules of H_2SO_4 used depends on the sulfate ions in final combination with Fe^{+3}, Mn^{++}, and K^+. The difference between the hydrogens required by HNO_3 and $KHSO_4$ and those supplied by the H_2SO_4 leads to the coefficient for water. Admittedly, one is not likely to solve this problem *by inspection*, but the process just outlined stepwise yields the following solution:

$$10\ K_4Fe(CN)_6 + 122\ KMnO_4 + 299\ H_2SO_4 \rightarrow 162\ KHSO_4 + 5Fe_2(SO_4)_3 + 122\ MnSO_4 + 60\ HNO_3 + 60\ CO_2 + 188\ H_2O$$

The majority of oxidations encountered in undergraduate work can be solved by the steps shown by the examples of the previous section. The student can find countless examples involving unsaturated hydrocarbons, alcohols, and aldehydes to test the method and to develop skill in its application.

Summary

Once all the materials involved in a reaction have been determined

$$(C_2H_5{-}S{-}H + HNO_3 \rightarrow C_2H_5{-}SO_3H + NO + H_2O)$$

the balancing of the equation can be completed by taking the following steps:

(1) Determine the change in oxidation number of the oxidizing agent.

$$(HNO_3 \rightarrow NO;\ 5 \rightarrow 2)$$

(2) Write a balanced equation showing the conversion of the oxidizing agent to the usual product(s) plus the appropriate number of free radicals.

$$(HNO_3 + H_2O \rightarrow NO + 3\cdot OH)$$

(3) Compare the structure of the organic reactant with those of the products, to determine the bonds to be broken.

$$(C_2H_5{-}S \text{ ------- } H \rightarrow C_2H_5{-}SO_3H + H_2O)$$

(4) Use one free radical for the breaking of a covalent bond which leads to an organic free radical

which, in turn, dimerizes, as in the formation of a disulfide.

$$(C_2H_5—S \cdots\cdots H + \cdot OH \rightarrow H_2O + C_2H_5—S\cdot)$$
$$(2C_2H_5—S\cdot \rightarrow C_2H_5—S—S—C_2H_5)$$

In all other cases, use two free radicals for the rupture of a covalent bond. This covers most organic reactions.

$$(C_2H_5—S—H + 2 \cdot OH \rightarrow C_2H_5—S—OH + H_2O)$$

(5) Use two free radicals for the formation of each new coordinate covalent bond.

$$(C_2H_5—S—OH + 4 \cdot OH \rightarrow C_2H_5—\overset{\overset{HO}{\diagup}\ \ \overset{OH}{\diagdown}}{\underset{\underset{HO}{\diagdown}\ \ \underset{OH}{\diagup}}{S}}—OH)$$

(6) Allow for the loss of water from structures which do not permit more than one hydroxyl group on a common atom.

$$(C_2H_5—S(OH)_4—OH \rightarrow 2H_2O + C_2H_5—\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}—OH)$$

(7) Complete the operation by the usual exchange of coefficients, removal of excess material found on both sides of the equation, and division by any common factor.

$$(C_2H_5—S—H + 2HNO_3 \rightarrow C_2H_5—SO_3H + 2NO + H_2O)$$

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Generalized Restatement of Coordination Rules

The possible types of coordination arrangement in crystals were treated from a topological viewpoint first by Niggli and Nowacki (*1*) and recently in more general fashion by Wells (*2*). Some restrictions to these possible structures for the case of ionic bonding are stated in Pauling's (*3*) Rules, which have been widely used for both the solution of structures and the instruction of students. The following considerations attempt to unify one aspect of these viewpoints. While these considerations are elementary, it seems desirable to make a clear statement of the implicit relationships. In this form the rules are more easily understood and applied by the student.

Consider atoms of types 1, 2, 3, ... m, . . . n. . . . , of proportions p_1, p_2, . . . p_m, . . . p_n in a crystal structure. In a topological representation, points representing these atoms may be connected by lines or links. If the configuration of links is fixed, then the number of connections coming to an m point from an n point is designated c_{mn}. Inasmuch as each such link must end on both an m and an n point,

$$p_m c_{mn} = p_n c_{nm} \tag{1}$$

because it does not matter which end of a link we count in getting the total number of links. The relation is very general, but if we link only pairs of atoms that are presumed to be bonded to another (such as the "ligands" of Pauling (*4*), or "structons" of Huggins (*5*)) then c_{mn} in equation (1) is the *coordination number of n around m*, irrespective of the nature or strength of such bonding. If connections are made only to nearest neighbors, then equation (1) gives the coordination numbers in their usual sense, that is, the numbers of nearest neighbors. The above equation is generally applicable to any crystal structure regardless of bond type.

In compounds whose bonding is principally ionic, the proportions must of course be related to the sums of positive and negative ionic charges, v_m and v_n, by virtue of over-all electrostatic neutrality:

$$\Sigma_m p_m v_m = \Sigma_n p_n v_n \tag{2}$$

With a single type of negative ion of charge v_x, this becomes

$$v_x = \Sigma_m v_m p_m / p_x \tag{3}$$

which by substitution of equation (1) becomes

$$v_x = \Sigma_m v_m c_{xm} / c_{mx} \tag{4}$$

If now connections are restricted to nearest neighbors, the c's become coordination numbers and equation (4) reduces to Pauling's "Second Rule": ". . . .The electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the center of the polyhedra of which it forms a corner. . ." Hence the requirement of electrical neutrality has been sharply localized.

The use of equations (1) or (4) presupposes a knowledge of some of the coordination numbers, the remainder being solved by the equations. It has generally been assumed, as stated by Pauling (*3*) in his "First Rule" that (1) *the coordination of large ions around small ions, or anions around cations, is determined by the radius ratio*, with large size cations in larger holes. However, in an ionic structure, if the neutralization of charge is to be sharply localized

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around the cations, just as it is localized around anions to get Pauling's Second Rule (e.g., 4), then we have Verwey's (Verwey and Heilmann (6)) "Principle of Maximal Charge Neutralization": (2) *The coordination of anions around cations is determined by the charge of the cation*, with cations of large charge in large holes. In some structures these two principles are at cross-purposes, as highly charged ions are generally small. Verwey demonstrated by both theoretical calculation and experiment that the second consideration usually overweighed the first in the determination of cation distribution in spinels. Verwey and also Goodenough and Loeb (7) also showed that the directivity of any covalent bonds may play an even more determinative part: (3) *The coordination of certain ions is determined by their covalent interbond angles.*

We cannot say *a priori* as to which of these three effects will dominate. However, once this point is determined or assumed we may apply equations (1) or (4). In the simplest cases, it does not matter which way we proceed. For example in fluorite, CaF_2, Ca fits in 8-coordination, so to find the coordination of F by equation (1),

$$c_{xm} = c_{mx}p_m/p_x = (8 \times 1)/2 = 4$$

or by using ionic charges in equation (4),

$$v_x = v_m c_{xm}/c_{mx},$$

whence

$$1 = (2 \times c_{xm})/8 \text{ and } c_{xm} = 4$$

In a composition that is slightly more complicated, but still has only a single type of anion, equation (1) still gives the result directly. In a compound like $Y_2{}^{+3}Z^{++}O_4$ (such as Al_2MgO_4), where Y is 6-coordinated and Z is 4-coordinated,

$$c_{oy} = c_{yo}p_y/p_o = (6 \times 2)/4 = 3$$

and

$$c_{os} = c_{so}p_s/p_o = (4 \times 1)/4 = 1$$

which is fulfilled by the spinel structure (of the type customarily designated "normal").[1] If, on the other hand, we had used equation (4), we would have had to find two unknowns in the equation

$$v_o = (v_y c_{oy}/c_{yo}) + (v_s c_{os}/c_{so})$$

or

$$2 = (3 \times c_{oy})/6 + (2 \times c_{os})/4$$

By using this equation we have discarded the independence of the two equations (1), that led to a direct solution in the first instance.

Very complicated structures, such as those of certain silicates, might be difficult to treat by equation (1). The difficulty lies not in any failure of the equation, but in the necessary subdivision of the oxygen ions into types that have the same cation coordination. Here it may be necessary to fall back on local charge neutralization and Pauling's Second Rule. In some cases the charge neutralization is not sufficiently localized to be determinative of the structure and this approximation fails.

Literature Cited

(1) Niggli, P., "Lehrbuch der Mineralogie und Kristallchemie," 3rd ed., Borntraeger, Berlin, **1941**, Vol. 1, p. 227.
(2) Wells, A. F., *Acta Cryst.*, **7**, 535, 842 (1954); **8**, 32 (1955).
(3) Pauling, L., *J. Am. Chem. Soc.*, **51**, 1010 (1929).
(4) Pauling, L., *J. Am. Chem. Soc.*, **69**, 542 (1947).
(5) Huggins, M. L., *J. Phys. Chem.*, **58**, 1141 (1954).
(6) Verwey, E. J. W., and Heilmann, E. L., *J. Chem. Phys.*, 15, 174 (1947).
(7) Goodenough, J. B., and Loeb, A. L., *Phys. Rev.*, **98**, 391 (1955).

[1] The nomenclature is analogous to that used above, i.e., c_{oy} is the coordination of y around o, etc.

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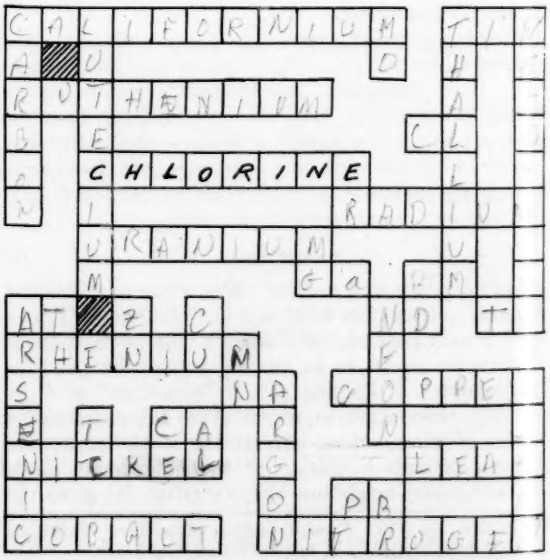
Skeleton Puzzle

Elements

The names and symbols listed below can be fitted into the diagram in only one way. One word has been inserted as a starting clue. Solution next month.

~~Al, At, Be, Ca, Ce, Cl, Cu, Er, Mg, Ga, Mn, Mo, Na, Nd, Pb, Pd, Pm, Pt, Te, Th, Tm, Zn~~
~~Tin~~
~~Lead, neon~~
~~Argon, radon~~
~~Carbon, cobalt, copper, nickel, radium~~
~~Arsenic, rhenium, uranium~~
~~Chlorine, Lutecium, nitrogen, thallium~~
~~Neodymium, ruthenium~~
~~Californium~~



Sister Helene Ven Horst
and **Helen Tang**
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Davenport, Iowa

Use of the Densitometer for Photometric Measurements

The densitometer is generally considered to be somewhat of a specialized instrument due to its limited use chiefly in the areas of paper chromatography, electrophoresis, and in the analysis of films. The authors have made use of this instrument for these purposes but have likewise used it with success in such analyses where the photometer is commonly used. The advantages of this modified photometer include the following: (1) a minimum amount of solution is required for any one analysis; (2) no special cuvettes are required; (3) minimum amount of time and work are required in converting the densitometer into a photometer; and (4) the time for an analysis does not exceed that required in the usual photometric procedure.

A model 525 Photovolt densitometer, a Varian recorder, and a decade box were connected according to the wiring diagram in Figure 1. The densitometer

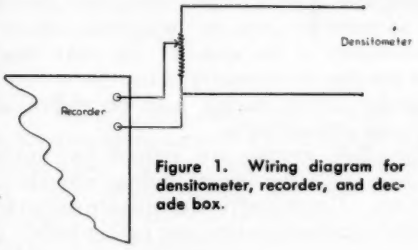

Figure 1. Wiring diagram for densitometer, recorder, and decade box.

was modified in the following manner in order to accommodate a short piece of 7-mm o.d. glass tubing which contained the solution being analyzed. The original paper guide and aperture plate were replaced with a piece of heavy cardboard which fit closely against the arm rest and evenly with the edges of the top of the densitometer. A 7-mm square was cut in the cardboard so as to be directly above the light source and in line with the photoelectric cell in the search unit of the densitometer. Two 1-cm thick felt strips, 10-cm long (cut from a blackboard eraser), were glued to the cardboard to form a kind of channel for the tubing. This framework was covered with another piece of cardboard which was also provided with a 7-mm square opening positioned in line with the aperture in the lower cardboard. In order to eliminate any stray light a piece of closely woven black cloth covered the entire surface of this apparatus with the exception of the square aperture. Such an arrangement also provided an easy means for changing the tube without disturbing the position of the aperture. One end of the glass tubing was sealed to a small funnel and the other was connected to a piece of rubber tubing which led to a waste jar. By placing a pinchcock on the rubber tubing it was possible to regulate or stop the flow of solution, either for purposes of analysis or in order to introduce a new solution. A diagram of this apparatus is given in Figure 2. In the analysis of any particular solution, appropriate narrow band-pass filters were inserted into the search unit of the densitometer containing the photoelectric cell.

The effectiveness of this modified colorimeter was determined by analyzing serial dilutions of various colored solutions according to standard procedures. The results are given in Table 1.

Table 1. Recorder Response for Serial Dilutions

Solution	Concentration range (gammas/ml)	Wave length of filters (mμ)	Range of recorder response
Nickel with dimethylglyoxime	0.3 to 5.0	445	6 to 92
Iron with 1–10 phenanthroline	1.0 to 5.0	505	2 to 97
Manganese as permanganate	1.7 to 8.5	550	12 to 91
Phosphorus as molybdophosphate	0.8 to 13.3	615	8 to 93

In all these cases there resulted a linear relationship by plotting the recorder response for the serial dilutions of the standards versus concentration. The order in which the serial dilutions were analyzed did not affect the results. In some cases the order of concentrations was increased; in others the order was reversed. Flushing the tube with the solvent did not alter the

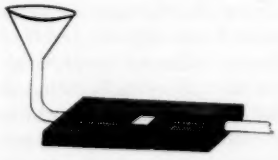

Figure 2. Attachment used in converting densitometer for use in liquid photometry

results, provided that when the solution was being analyzed a sufficient amount (3 ml) of the solution was added to bring the recorder response to a constant reading.

In an effort to compare the readings obtained on the Bausch and Lomb spectrophotometer with those of the modified densitometer, standard curves were prepared from the data shown in Table 2. Equal volumes (3 ml) of serial dilutions of iron with 1–10 phenanthroline were analyzed at a wave length of 505 mμ. Since no special effort was made to duplicate the readings by adjusting the resistance of the modified

densitometer, the results may not seem to be in good agreement; however, it is to be noted that the slopes of these curves are nearly identical.

It is apparent that with a minimum change in the densitometer this instrument is readily adapted for use in photometric analyses. This modified instrument has its advantages, primarily that of its extended use in the laboratory and the absence of any cost in making the modification.

The authors gratefully acknowledge the financial assistance of the American Academy of Arts and Sciences.

Table 2. Comparison of Absorbance of Spectrophotometer and Recorder Response of Modified Densitometer in Analysis of Iron with 1–10 Phenanthroline

Concentration (gammas/ml)	Absorbance[a]	Recorder[b] response
1	0.24	0.28
2	0.45	0.53
3	0.68	0.74
4	0.90	0.97

[a] Slope of curve plotting absorbance vs. concentration 0.227.
[b] Slope of curve plotting recorder response vs. concentration 0.225.

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Simplified Models of Inorganic Stereoisomers

A recent paper by Myers[1] in THIS JOURNAL has shown the modification of inexpensive commercial models to illustrate metal coordination compounds. With a few simplifications, such models are readily adapted to the depiction of stereoisomers of inorganic complexes.

Scale models such as the Fisher-Hirschfelder-Taylor Metal-Coordination Atom Model Kit[2] are ideal for research, since they accurately picture interatomic angles and distances, molecular sizes, steric hindrances, etc. They are also suitable for small classrooms. However, their cost and small size make them far less suitable for use with large undergraduate classes. Also, the compactness of the structure and the intricacy of the ligands complicate the issue by distracting the beginning student from the basic problem, viz., the arrangement of the ligands around the central atom.

The present author also uses the Sargent Organic Structure Model Set[3] suggested by Myers, but for central metal atoms (square planar, octahedral, tetragonal pyramidal) he uses the rubber balls included in the Fisher Master Crystal Model Set[4] with which hole-drilling is unnecessary. To show unusual hypothetical configurations such as hexagonal planar or trigonal prismatic, additional holes can be easily made by using a No. 2 cork borer.

The ligands are represented simply by differently colored balls. No attempt is made to show the structure of these ligands as was done in the models described recently by Wendlandt[5] and Myers.[1] The purpose of the proposed models is to demonstrate stereoisomerism only. Ligands are therefore depicted as simply as possible, consistent with their effects on the stereochemistry of the system. To make clear to the student the degree of simplification, one or two Fisher-Hirschfelder-Taylor models may be shown next to their simpler counterparts.

Multidentate groups are formed by linking the ligand balls with the helical springs provided in the Sargent set. Unsymmetrical groups are shown by using differently colored ligand balls or rubber balls.

In most inorganic chemistry courses, proof of configuration by number of isomers is an important topic. The method consists of assuming the most likely configurations in which the equivalent groups can be symmetrically arranged about a common center, predicting the number of possible arrangements for compounds of different types for each of these configurations, and comparing this number with the number of isomers actually prepared. This classic example of an indirect method of structure proving can be effectively presented with these models (Fig. 1).

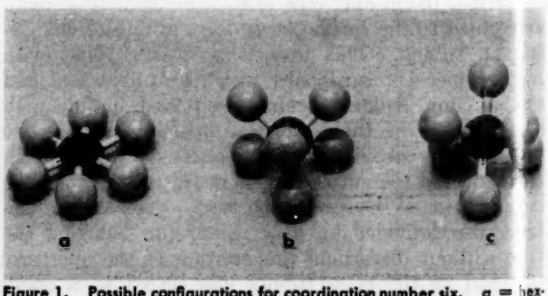

Figure 1. Possible configurations for coordination number six. a = hexagonal planer, b = trigonal prismatic, c = octahedral.

[1] MYERS, R. T., J. CHEM. EDUC., **35**, 152 (1958).
[2] Fisher Scientific Company, Pittsburgh, Pa. Catalogue No. 12-822.
[3] E. H. Sargent and Company, Chicago, Ill. Catalogue No. S-61815.
[4] Fisher Scientific Company, Pittsburgh, Pa. Catalogue No. 12-816.
[5] WENDLANDT, W. W., J. CHEM. EDUC., **34**, 223 (1957).

The two-dimensional representations of the configurations for coordination number six commonly found in textbooks are apt to be misinterpreted by the student. They emphasize the "outer structure" and do not point out that the bonds are directed from the central atom toward the ligands (contrast with Figure 1). For example, there is a distinct difference between the hexagonal planar structure and the benzene ring. Also, the conventional representation of the octahedron may give students the impression that the upper and lower positions are different from the four positions at the corners of the square. Such misconceptions are less likely to arise when the proposed models are used.

Optical isomerism as well as geometric (*cis-trans*) isomerism can be demonstrated. Unsymmetrical chelate groups can be illustrated as shown in Figure 2*a*, while a slight modification allows the depiction of an unsymmetrical chelate group which is itself optically active (Fig. 2*b*). Chelate groups are not limited to bidentate ligands; as a case in point, a compound containing a sexadentate group recently synthesized by F. P. Dwyer is shown in Figure 2*c*.

The models are not limited to depicting mononuclear complexes. Binuclear and polynuclear complexes can also be shown.

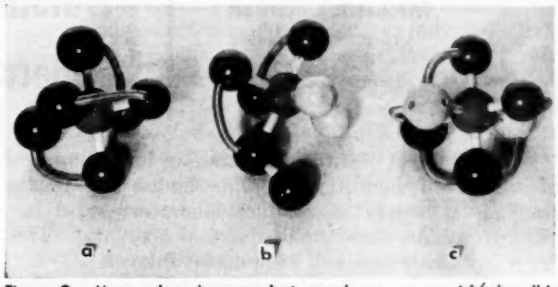

Figure 2. Mononuclear hexacovalent complexes. *a* = *tris*(phenylbiguanidine)cobalt(III) ion, $[Co(\phi BigH)_3]^{+3}$ (one antipode), *b* = *cis*-dinitro (ethylenediamine)(propylenediamine)cobalt(III) ion, *cis*-$[Co\ en\ pn(NO_2)_2]^+$ (one of eight forms), *c* = 3,6-dithia-1,8-bis(salicylideneamino)-octanecobalt(III) ion, $[Co(C_{20}H_{22}N_2O_2S_2)]^+$ (one antipode).

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A Simple Rapid Method for Loading Paper Chromatograms

The usual method of loading paper chromatograms involves applying 1 to 5 μl of sample onto the origin with some type of capillary micropipet. In addition, some special drying apparatus is usually employed to restrict the size of the spot and shorten the interval between applications. Even so, it is quite laborious to load more than a few μl onto a chromatogram and difficult to produce small, uniform spots. These requirements and difficulties can be reduced by the use of small paper discs, saturated with the sample to be analyzed, dried, and affixed to the origin of the chromatogram.

Discs 6 mm in diameter can be made from chromatography paper with an ordinary paper punch. Such discs have a very uniform saturation capacity and take up approximately 3 μl when touched to the surface of a solution.

A convenient procedure for using such a disc is to transfix it with a straight pin, touch it to the surface of a test solution, stick the pin into a cork, and allow the disc to dry. The disc may then be affixed to the chromatogram by making two short, parallel slits about 2 mm apart at the desired origin and slipping the disc between the strip thus formed and the main body of the chromatogram. The uniform saturation capacity of such discs permits quantitative comparisons between the results obtained from discs saturated in different solutions.

Alternatively, larger volumes of solution can be loaded quite rapidly onto the disc by the following

procedure. The disc is transfixed with a straight pin so that it is at the end opposite the point. The pin is then thrust into the underside of some surface or a cork so positioned that the pin is vertical but the disc carrying end is the lower. Any pipet calibrated in 0.01 ml units can then be used to allow up to 50 μl to flow onto the disc. A pendulant droplet may form on the disc, but dripping will not occur if no more than 50 μl is added. The disc can then be allowed to air dry or a hot plate can be positioned a few inches below the disc to hasten the drying. The dried disc is then attached to the chromatogram in the manner described.

This technique has given particularly satisfactory results when used in conjunction with circular chromatography. Two views of such an assembly are shown in the illustration, which also illustrates the general manner of disc attachment. The disc is affixed a few mm below the apex of a triangular wick. The wick apex is then inserted through a small slit (2–3 mm in length) in the center of the circular chromatogram, and the assembly is placed on the solvent-containing Petri dish in the manner illustrated. Superior resolution can be achieved with only a minimum of experience.

Journal paper No. 145, American Meat Institute Foundation.

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Training Teaching Assistants for General Chemistry

At institutions handling large numbers of students in chemistry programs the use of graduate teaching assistants to conduct laboratory—and less often recitation—sections is a virtual necessity. This has many advantages and a few disadvantages.

To the graduate assistant it provides an excellent opportunity to review and fix certain chemical principles in his mind; it provides him an opportunity to learn to express himself clearly and concisely; it assists him financially; it permits him to develop leadership, and it gives him an opportunity to help young scientists. On the other hand, graduate students usually lack experience both in teaching techniques and in handling the subject matter; they have what is undoubtedly a more compelling motive than teaching—they must pass their graduate courses. These factors often decrease the effectiveness of programs involving graduate assistants. One way to improve this situation is to subject all teaching assistants to a vigorous training program which begins before they actually start teaching and continues throughout most of their tenure.

In planning such a program it is important to recognize clearly some of the important functions of the teaching assistant. Four of these are:

(1) To make close contacts with students.
(2) To help cement principles of chemistry in students' minds.
(3) To cultivate observation and interpretation.
(4) To teach laboratory techniques.

All of these functions are obvious and require no elaboration, but they will serve as useful guideposts not only for the training segment but in planning and conducting all aspects of the general chemistry program.

For convenience this training program may be divided into formal and informal portions. The formal portion should include an orientation program, regular staff meetings, attendance at lectures, and some on-the-job training. The informal portion should consist of machinery whereby the teaching assistant is enabled and encouraged to have conferences with senior staff members as often as necessary. This point cannot be overemphasized. The attitude of the teaching assistant toward his students is very often a reflection of the attitude of the senior staff toward the teaching assistants.

Orientation

The orientation program is especially important and is a must for new assistants. Several universities devote portions of the week preceding the opening of classes in the fall to a series of discussions, tours, and demonstrations designed to prepare staff members to handle their assignments. A good orientation program should include:

(1) The philosophy of the course and possibly of the entire general chemistry program of which the assistant will be a part.

(2) The role of the teaching assistant in this program.

(3) Some information about the handling of students.

(4) Some essential teaching techniques.

(5) Some standard operating procedures for the laboratory under consideration.

Following is an outline of a series of five discussions which constituted portions of the orientation programs for new teaching assistants at Ohio State University, Michigan State University, and University of Florida.

Discussion I. General Organization
- (A) An over-all view of the general chemistry program
  - (1) Answer each of these questions:
    - Whom are we trying to teach?
    - What are we trying to teach?
    - Why are we trying to teach it?
  - (2) Nature and structure of various general chemistry courses offered by this department
- (B) Standard operating procedures in this laboratory
  - (1) Mechanical:
    - Storeroom arrangements and procedures
    - Treatment of laboratories and equipment
  - (2) Pedagogical:
    - Approach to problem solving to be used in this department
    - Methods of balancing equations
    - Conventions regarding mole concept, definitions of oxidation-reduction, etc.

Discussion II. Conducting Recitation and Laboratory Sections
- (1) Establishing rapport
- (2) Personal contacts with students—individual teaching
- (3) The value of a lesson plan
- (4) Set an interesting, learning atmosphere
- (5) Actually demonstrate operation of a recitation class
- (6) Simulate a laboratory session.

Discussion III. Some Important Teaching Techniques
- (1) The question-answer-discussion method
- (2) The drill-sheet method—each student works at his own speed
- (3) How to demonstrate
- (4) Special techniques for beginning and ending laboratory and recitation classes

Discussion IV. Laboratory Safety and First Aid
- (1) Require all assistants to learn material in "Handbook for Teaching Assistants"
- (2) Location of First Aid equipment in laboratories and how to use it
- (3) Tips on accident prevention
- (4) What to do in case of accident

Discussion V. Evaluating Student Ability and Performance
- (1) The obligation to know each student
- (2) Preparation of tests, grading, reports
- (3) Criteria for personal evaluation

Presented as part of the Symposium on Problems of Teaching Large Laboratory Sections before the Division of Chemical Education at the 131st Meeting of the American Chemical Society, Miami, April, 1957.

Several schools report that excellent results were obtained by supplementing orientation programs with talks presented by suitable representatives of the College of Education. In addition, it is the custom during the orientation program at Michigan State to have each new teaching assistant perform one of the experiments from the laboratory manual under the exact conditions and using the same equipment to be used later by his students. This assistant, in addition to familiarizing himself with the laboratory operation, is in a position to brief other members of the staff on the fine points of the experiment he performed. This briefing is usually given at the staff meeting preceding the lab period in which that particular experiment is scheduled.

As a substitute for the verbal orientation program, many schools distribute copies of the "Handbook for Teaching Assistants"[1] to all new assistants and require that they be familiar with its contents before entering the classroom or laboratory. Perhaps the best plan is to provide copies of the handbook in addition to the discussion.

Staff Meetings

The second phase of the formal program is regular staff meetings and attendance at lectures. This, a necessity for a successful program, is a mechanism to assure clarity and reasonable uniformity of subject matter presentation. In addition it provides an opportunity to discuss special aspects of each experiment and of each phase of the subject matter. Finally it is a useful device for "feeling the pulse" of the students and staff. This latter point—controlling student and staff morale—often makes the difference between a mediocre and a good general chemistry program.

Various devices are used to make these staff meetings tools for training the assistants. Several top-flight teachers devote a portion of the staff meeting to asking questions of the assistants similar to those students might be expected to ask. Others make each student responsible for discussing a particular laboratory experiment while still others devote a portion of certain staff meetings to preparing quizzes or portions of examinations, requiring the assistants to supply questions or ideas for questions.

On-the-Job Training

The third phase of the training program, on-the-job training, is a must for improving performance, yet it is the most difficult to implement. These young teaching assistants need help and encouragement during the early stages of their development. Each has his own problems to solve and, while each should be given considerable freedom in solving these problems, gentle guidance and support at the right moment will strengthen confidence and improve judgment in a most gratifying manner. This guidance can only be provided by experienced teachers. Hence it is incumbent upon the senior staff to work with the teaching assistants in laboratories and recitation sections and to share their experience and enthusiasm with these young people.

This problem is so well recognized that there are at least a dozen plans now in operation at various universities designed to give on-the-job training to teaching assistants. Several schools require all members of the general chemistry staff to spend a portion of their time with the assistants in recitation and laboratory. In one case each staff man is assigned a group of recitations and laboratory sections. In addition he is given several teaching assistants. The idea is that the senior staff member is to train the assistants to handle these sections. Conscientious teachers in this system believe this is effective.

A highly successful extension of this idea is that of making each lecture section of a large course completely independent of all other sections. Thus the students in this section take laboratory together and have recitation at the same hour. In this system the teacher in charge of the section not only has maximum control over students in his section but he works closely with a small group of assistants.

Another successful plan is to assign several experienced teachers as laboratory supervisors. These individuals spend all of their time seeing that the laboratory operates smoothly and helping the assistants do a better job of teaching.

The suggestions detailed in these paragraphs do not constitute the ultimate in training teaching assistants. However, they have met with considerable success and most persons who have seen the results of such training will never "turn assistants loose" in the laboratory or recitation without some preparation. Finally, the essential point of this article is that training programs are vital; that they can be worked into the over-all program without major schedule revisions, but that in order to be successful they must be planned and in perpetual operation.

Acknowledgment

The author wishes to thank Professor A. B. Garrett for suggesting this topic and both Dr. Garrett and Professor F. B. Dutton for many of the ideas suggested herein.

[1] Published by the Handbook Committee of the General Chemistry Workshop of the Committee on Teaching of College Chemistry, the Division of Chemical Education of the American Chemical Society. Copies are available from Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pa.

Dates. . .

April 1–4 National Science Teachers Association in Atlantic City

April 5–10 American Chemical Society in Boston, Massachusetts

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Corvallis

Excessive Use of Graduate Assistants in Recitation and Laboratory Teaching

An exchange of correspondence

In years gone by, career instructors and professors did most of the teaching to freshman chemistry students—in lectures, recitations, and laboratory sections. As the number of students taking first year chemistry has increased, and as the number of graduate students has also increased, a different teaching assignment program prevails in most colleges and universities. Graduate assistants, often called teaching fellows, do a high percentage of the recitation and laboratory teaching. The desirable increase in enrollment in chemistry at both the freshman and graduate levels and the trend of professors to spend much of their time on research or upper division and graduate teaching have resulted (this author believes) in lessened teaching efficiency to beginning chemistry students. Accordingly, the following letter was sent to several prominent teachers (some, authors of textbooks) at large colleges and universities throughout this country. The replies are typical of many received.

Dear Dr.:

For some years I have felt our recitation and laboratory instruction in freshman chemistry has been becoming less efficient for the following reasons:

(1) About 80% plus of our recitations are handled by graduate assistants.

(2) Too often we do not get to keep the better graduate assistants as teaching fellows. (Research assistantships are more profitable or desirable and if we have a man for a year or two and he proves himself, he is often offered a desirable research assistantship.)

(3) We have a high turnover in assistantships—many graduates are only here through M.S. degree.

(4) In our chemistry courses of lecture, recitation, and laboratory, students for the most part have three instructors involved (a staff member lecturer and 2 different graduate assistants). The graduate assistants, because of class scheduling difficulties, many times do not get to the lecture.

(5) There is no scheduled full-time staff supervision for 30 of the 36 hours we have freshmen in laboratory. The assigned staff hours are complied with by stroll through the laboratory and office availability.

(6) There is a one-hour meeting a week for lecture professors to meet and coordinate the week's work (this usually lasts 30 minutes). An outline of subject coverage is given, but no "how to teach" program is involved.

I believe 60% or less recitation sections should be taught by graduate assistants, and that some instructor or above should be in charge of each laboratory time (4–5 sections in lab.)—actually doing some strolling, teaching supervision. I believe most large schools are as extended toward graduate assistant teaching as we are. Will you suggest briefly how your chemistry department program operates as regards freshman chemistry teaching.

Based on a paper presented before the Division of Chemical Education at the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958. Published with the approval of the Publications Committee, Oregon State College, as Research Paper No. 342, School of Science.

Reply from a western university:

In our principal course there are three lectures per week, one hour of recitation and two laboratory periods of two hours each. A permanent member of the staff gives the lectures and he is responsible for the laboratory and recitation. However, the actual teaching in these sections (of about 20 students) is by graduate students. The same graduate student usually handles both recitation and laboratory. The professor writes all tests. *Most of our teaching assistants are first year graduate students. A few are kept on teaching for two years.* Once each week the professor and teaching fellows confer for 30 minutes to one hour.

A part of the teaching load of an associate professor is the supervision of laboratory sections in general chemistry. He keeps the teaching assistants in line and they must report to him when they are not able to meet a class, etc. He teaches no sections but is frequently in the laboratory, and he does much to see that things run well. We also have two advanced teaching assistants (graduate students) who in effect are assistants. One of them is present when the laboratory is in operation and he helps the new teaching assistants (there may be as many as eight at a time) do a good job.

I believe that the quality of instruction in general chemistry here could be improved by assigning a regular member of the staff to lecture in only one course but to have him also take a recitation section and a laboratory section. He should be assisted by a graduate student while in the laboratory so that he could spend part of his time visiting the other sections then in operation. He should be expected to be at work in the laboratory all of the time while his section is at work. This would make the lecturer much more aware of things which should be done in recitation and laboratory. One can see from examinations which we give now that some of the lecturers scarcely think about the laboratory. They ask practically no questions about the exercises.

You have the right idea, and I wish you success in your efforts to improve the situation.

Reply from a midwestern university:

We have currently a senior staff of three full professors, one assistant professor, and four instructors in charge of our freshman work. Each of the professors handles advanced inorganic work but has a certain amount of freshman teaching. This semester we are offering eight different freshman courses, for each at the first and second semester levels. These courses vary per week from six hours of laboratory, two hours of quiz, two hours of lecture for five credit hours and two hours of laboratory, two hours of quiz, and two hours of lecture for three credit hours. Each course is supervised by a senior staff member who plans the lectures and handles all of the details of the teaching staff. Some of the courses have several lecture sections with more than one lecturer. The laboratory and quiz sections are almost completely handled by graduate assistants—with only a few being taken care of by instructors. Quiz and laboratory sections are split between two assistants only when scheduling difficulties render such arrangements unavoidable. Primary supervision by the senior staff is effected through weekly staff meetings in each course and through unscheduled visits to quiz and laboratory meetings. There is no formal patrolling of the laboratories. Each assistant is graded (1 = excellent through 5 = fired) at the end of each semester, and these grades are made part of his graduate record.

Actually, we give our assistants a very large amount of responsibility, and I must say that most of them accept it very

well indeed and work conscientiously and effectively. We lose most of our best people to fellowships and research appointments after a year, but a few stay on to provide nuclei for subsequent years. With a few very rare exceptions, the quality of assistant instruction has been good in the 15 years or so that I have been here. In some cases, it has exceeded that offered by our instructors. My major criticism is lack of direct laboratory supervision, and I have suggested several times that each of us on the senior staff take an hour or two a week of our own time for just this.

All in all, I am in favor of a graduate assistant type of system with close senior staff supervision and senior staff participation in laboratory and quiz section groups. I have argued for some time that the best teachers in the department are needed at the freshman level and that any competent and interesting man in the department, regardless of his field of specialization, should handle some freshman classes.

Reply from a midwestern university:

Of a total of 65 quiz sections in our various general chemistry courses, 58 (89.3%) are run by graduate teaching assistants, and only seven (or 10.7%) by instructors or higher. All of our laboratory sections are run by graduate assistants. No instructor, or higher, is specifically assigned to laboratory supervision. We do, however, stroll through the laboratory at frequent intervals when we are free. About 50% of our students have a different teacher in laboratory and quiz.

We feel, as you do, that we should have several full time instructors. Recruitment of good graduate teaching assistants is getting tougher every year; biggest competition comes from the research assistantships and fellowships. Our best grad students seldom teach more than a year or two; they are awarded research fellowships. We are as concerned as you but the budget is so tight that there is no good solution in sight.

Reply from a western college:

We have a full-time staff member in charge of each of the laboratory groups. This instructor is assisted by from two to eight or so laboratory assistants. The instructor in charge of the laboratory not only supervises the running of the laboratory but participates in the instruction of students as well. He is available at all times during this laboratory period for consultation with students. We have tried to maintain a policy of having most of our tutorial or recitation sections in charge of a full-time staff member, since we have found that many of the graduate assistants are too inexperienced or are not competent to handle tutorial sections in the manner which they deserve.

One of our big problems in the freshman program is obtaining sufficient teaching fellows to handle small laboratory sections which run about 25 students per section. We find it necessary to use graduates from other departments of the college; for example, botany, pharmacy, horticulture, etc., and in addition it is necessary to employ some undergraduates for laboratory assisting. The latter are not always very satisfactory. A meeting of the laboratory assistants is held once each week to discuss laboratory work coming up the following week. Full-time staff members teaching inorganic chemistry also meet once a week.

During the first semester work practically all of our recitation or tutorial sections are handled by full-time staff members. We feel sure that the tutorial sections have been taught in a much more competent fashion and criticisms by students of the tutorial sections have been much less than in previous years when we were using graduate assistants for this purpose. Some of the teaching fellows do a very good job in tutorial but again many are not qualified to handle these sections.

Conclusions

In recent years, a high percentage of recitation and laboratory teaching has been, and is being, done by graduate assistants in freshmen chemistry. Teaching efficiency cannot be had with the marked man-power turnover inherent in use of graduate assistants. One does not find as much use of graduate assistant in classes in mathematics, English, engineering, etc. The very fine surge in research has had its repercussion in the use of freshman recitation and laboratory instruction as a job field for graduate students whose main interest is their own class work and research. Research money from industry and institutional grants is becoming more abundant to subsidize the research assistant; and the faculty that acquires research money can lessen the number of teaching assistants. Administrative personnel should be presented the actual facts on percentage of college and university chemistry teaching done by the new, inexperienced, short tenure, secondary interest, graduate assistant; and funds will be made available for employment of additional worthy full-time faculty members. Proper presentation of the facts has resulted in three new faculty members being added to the general chemistry teaching staff at the author's school; these men will also strengthen advance course offerings and research output.

New Translation of Arfwedson's Paper on Lithium Discovery

In 1818, about one year after the momentous discovery of lithium, Johann Auguste Arfwedson reported his work "Investigation of some minerals from the Utö mine and the discovery of a new fixed alkali" in the Swedish scientific journal "Afhandlingar i Fysik, Kemi och Mineralogi." The article was soon translated and appeared in Germany in Dr. Schweigger's "Journal für Chemie und Physik" (1818) and in France in "Annales de Chemie et de Physique" (1819).

However, no other translations were ever published. Searches in the Library of Congress, the Union Library Catalog of Philadelphia, and the New York Public Library have failed to turn up any subsequent versions. A new translation was motivated by this lack and by the historical importance of Arfwedson's work.

As a result, a complete version of this little known chapter from the annals of science was recently made by Norman P. Gentieu, Technical Writer, Foote Mineral Company. This translation can be obtained by writing to the Technical Literature Department, Foote Mineral Company, 18 West Chelten Ave., Philadelphia 44, Pa.

In "Discovery of the Elements" (Sixth Edition), Mary Elvira Weeks has written a superb account of Arfwedson and his work. Chapter 18, "Three Alkali Metals" gives some interesting historical background on lithium, while Chapter 19, "J. A. Arfwedson and his Service to Chemistry" is a good concise biography of the man.

The fact that lithium's remarkable properties went unrecognized and unappreciated for over a century does not lessen the importance of Arfwedson's "find." In the history of chemistry, the discovery of lithium will remain an invaluable heritage of the nineteenth century to our own time and ages yet to come.

Max S. Peters
University of Illinois
Urbana

A formal option plan for Undergraduate Chemical Engineering

In recent years, there has been an increasing amount of discussion among chemical engineering educators on the need for more "engineering science" in the undergraduate training program. The exact definition of "engineering science" is vague, but its general connotation is that emphasis should be placed on the basic disciplines such as physics, mathematics, and physical chemistry principles with a resulting de-emphasis on such "how-to-do" subjects as chemical technology, machine laboratories, and power laboratories.

Any proposals to revise and modernize our present undergraduate curricula in chemical engineering must recognize the fact that only about 25% of the graduating seniors go on to advanced study in graduate school. Consequently, an ideal curriculum must meet the needs of the 75% of the students who enter industry immediately after graduation and must also give the students who wish to enter graduate school a strong background for advanced study.

An attempt to meet these requirements has been made at the University of Illinois by a major revision of the undergraduate curriculum in chemical engineering. The revision is based on the use of two standard options. One of these, designated as the engineering option, is primarily for chemical engineers who intend to enter industry at the completion of the B.S. degree. The second, designated as the physical science option, is intended for those chemical engineers who expect to engage in advanced study and research beyond the B.S. degree. The options are designed for completion in a regular four-year program of two semesters per year, and 136 credit hours are required for graduation in each option.

First Two Years Same for Each Option

It is assumed that the students enter as freshmen with high school training in mathematics through trigonometry and college algebra, permitting them to start the first semester with analytic geometry. In this way, integral calculus is completed by the end of the first semester in the sophomore year. It is also assumed that the entering freshmen have had chemistry, physics, and two years of foreign language in high school.

In the regular curriculum, which is identical for each option during the first two years, the students complete 18 hours of chemistry by the end of the sophomore year. This includes three hours of physical chemistry and five hours each of general, qualitative, and quantitative chemistry. Also included in the first two years are three four-hour courses in physics, two courses in rhetoric, eight hours of foreign language, a three-hour course in engineering drawing, a course in analytical mechanics (Statics), four semesters of noncredit physical education and military, and four hours of humanities or social sciences electives.

Choice of Option Made at Start of Junior Year

At the start of the junior year, the student must indicate a choice as to which option he prefers. At least a "B" average is required in order to take the physical science option, and this choice is recommended for those students who intend to continue work in graduate school. If the student is not sure of his future plans, he is directed toward the engineering option with a strong recommendation that he choose differential equations and advanced calculus as two of his advanced technical electives. Because of the interest in bioengineering in the Midwest, a few students in the engineering option take a special series of bacteriology and biochemistry electives to give them an undergraduate training closely equivalent to that required for a normal Bioengineering degree.

Comparison of Options

The major difference between the two options is the amount of required advanced mathematics, physical chemistry, and physics. The physical science group must take at least six hours of mathematics beyond integral calculus, a course in atomic and solid-state physics, at least two extra hours of advanced technical elective, and an advanced course in physical chemistry beyond the seven basic hours required for the engineering option.

Table 1 presents a comparison of the requirements for the two options in the junior and senior years. It can be seen that the extra technical courses taken in the physical science option are compensated by a reduction in the amount of required electrical engineering, organic chemistry laboratory, chemical technology, thermodynamics, and mechanics laboratory

Electives

One of the major strong points of this new curriculum is the flexibility in the engineering option permitted by the choice of electives. A minimum of 24 hours of social science and humanities electives, including rhetoric and foreign languages, are recommended. This leaves 11 hours of additional electives to be chosen by the student. Although the students in the engineering option are urged to take differential equations (and 80 to 90% of them do take it), this course is not required. Some educators feel that this is a mistake and that no student should receive a bachelor's degree in chemical engineering without

taking differential equations. We believe that a B.S. chemical engineer who has no interest in advanced mathematics can still be a success in industry. Accordingly, we feel that there are individual cases where a student can benefit far more from an elective course in business administration, industrial engineering, or similar subjects which the student chooses than he would from a required course in advanced mathematics.

As the result of a requested revision in the electrical engineering service courses, it has been possible to reduce the amount of required electrical engineering in the physical science option while still giving an adequate background in the subject. A basic three-hour course in electrical engineering is required for all chemical engineers, and a strong recommendation is made that the students choose as advanced technical electives combined lecture and laboratory courses in Electronics and Electronics Applications, Electrical Instruments and Measurements, or Application and Control of Motors and Instruments.

This option program, which went into effect in the fall of 1958, is the result of discussions in many staff meetings during the previous years. The staff feels that it is essential to offer a program which will be a challenge and give the necessary training to the outstanding students who have the ability to make a real contribution to chemical engineering through advanced study and research. On the other hand, it is considered equally important to provide a solid practical training for the average student who, although he will probably never make any exceptional scientific contributions, will nevertheless be one of that essential group of engineers which makes up the backbone of our chemical industry. The staff at the University of Illinois feels that the option plan as presented here represents an excellent method for meeting the diverse requirements of an ideal undergraduate training program for the modern chemical engineer.

Table I. Courses in Options for Junior and Senior Years

Course	Engineering option	Physical Science option
Chemical Engineering		
Stoichiometry (3 hr.)	1 Sem., Jr.	1 Sem., Jr.
Instrumentation (2 hr.)	1 Sem., Jr.	1 Sem., Jr.
Thermodynamics (3 hr.)	2 Sem., Jr.	2 Sem., Jr.
Principles (4 hr.)	2 Sem., Jr.	2 Sem., Jr.
Principles (4 hr.)	1 Sem., Sr.	1 Sem., Sr.
Unit Operations Lab. (3 hr.)	1 Sem., Sr.	1 Sem., Sr.
Plant Inspection Trip (1 hr.)	1 Sem., Sr.	1 Sem., Sr.
Technology (3 hr.)	2 Sem., Sr.	...
Research Projects Lab. (2 hr.)	2 Sem., Sr.	2 Sem., Sr.
Plant Design and Economics (3 hr.)	2 Sem., Sr.	2 Sem., Sr.
Chemistry		
Organic (5 hr.)	1 Sem., Jr.	1 Sem., Jr.
Organic (3 hr.)	2 Sem., Jr.	2 Sem., Jr.
Organic 2nd Lab. (2 hr.)	2 Sem., Jr.	...
Physical Chemistry (3 hr.)	2 Sem., So.	2 Sem., So.
Physical Chemistry (4 hr.)	1 Sem., Jr.	1 Sem., Jr.
Advanced Phys. Chem. (3 hr.)	...	1 Sem., Sr.
Thermodynamics (2 hr.)	1 Sem., Sr.	...
Mathematics		
Advanced Calculus (3 hr.)	...	1 Sem., Jr.
Differential Equations (3 hr.)	...	2 Sem., Jr.
Physics		
Atomic and Solid State (3 hr.)	...	2 Sem., Sr.
Theoretical and Applied Mechanics		
Statics (2 hr.)	2 Sem., So.	2 Sem., So.
Deformable Bodies (3 hr.)	1 Sem., Sr.	2 Sem., Sr.
Solids Lab. (1 hr.)	1 Sem., Sr.	...
Electrical Engineering		
Basic (3 hr.)	2 Sem., Jr.	1 Sem., Sr.
Electronics, Machines, or Measurements (3 hr.)	2 Sem., Sr.	...
Electives		
Social Sciences or Humanities	4 hr. + 4 hr. in So. Yr.	4 hr. + 4 hr. in So. Yr.
Advanced Technical	6 hr.	8 hr.
Free choice	7 hr.	4 hr.

Chem Gems

Given: The equation of state for one mole of an ideal gas and Ohm's law for steady currents in metallic conductors.

To Prove: That "Very Important People are Egotistical Tyrants."

Proof:

$$PV = RT \tag{1}$$

$$E = IR \tag{2}$$

From (1)

$$R = (PV)/T \tag{3}$$

From (2)

$$R = E/I \tag{4}$$

Thus, equating (3) and (4)

$$(PV)/T = E/I \tag{5}$$

Rearrangement of (6) leads to

$$VIP = ET \tag{6}$$

thereby completing the proof.

Note: An alternative conclusion is possible. A rearrangement of (6) yields the prediction that "People in Venice are Turkey Eaters."

FRANK L. PILAR
University of New Hampshire
Durham

[EDITOR'S QUERY: Where have these been? The supply has evaporated to dryness—and we don't mean wit!]

Division of CHEMICAL EDUCATION
American Chemical Society

M. Gilbert Burford
Wesleyan University
Middletown, Connecticut
and **Harry F. Lewis**
The Institute of Paper Chemistry
Appleton, Wisconsin

The Wesleyan Conference of 1958

One approach or several?

In 1957, a conference was set up at Reed College by the Committee on Teaching of the Division of Chemical Education and under the sponsorship of the Crown Zellerbach Foundation to review some of the more important problems in the better integration of the teaching of chemistry in high schools and colleges.[1] Along with other matters, the Reed Conference expressed its dissatisfaction with high school texts in chemistry and its interest in the possibility of developing a new high school course based upon chemical bonding as a central theme.[2] A committee of conference members led by L. E. Strong of Earlham and M. K. Wilson of Tufts developed a tentative outline of such a course. Among the recommendations of the conference was that a follow-up conference be held in 1958 to take a fresh look at the Reed outline and its implications and to review the experiences of the two high schools which made some use of the outline in 1957–58.

A proposal for such a conference was then submitted to the National Science Foundation by Wesleyan University with the support of the Committee on Institutes and Conferences of the Division of Chemical Education. This was approved and the conference was held in Middletown, Connecticut, on June 16–26, 1958. There follows a short report on the Wesleyan Conference, its discussions, conclusions, and recommendations.

In order to bring to bear on the tentative course proposal of the Reed Conference the experiences of a different group of high school and college teachers, the Wesleyan Conference members consisting of seventeen high school, one junior college, and seventeen college teachers included only nine of the full-period conferees from the Reed group.

The plan of the conference was as follows: The first two days were devoted to informal talks by A. H. Livermore on the general outline of the Reed Conference; by L. E. Strong on the chemical bond as a central theme; by E. P. Little, Executive Director of the Physical Science Study Committee program for Secondary School Physics; and by Jose Gomez-Ibanez on the 1957 Johns Hopkins Conference. Later in the period, the conference heard from Howard Wagner, recently high school teacher of chemistry at the Laconia, New Hampshire, High School and Editor of the Newsletter of the New England Association of Chemistry Teachers; from Donald Anderson of the National Science Foundation on the program of the Section of Course Content and Improvement; from William Kieffer, Editor of the JOURNAL OF CHEMICAL EDUCATION; from John Baxter of the University of Florida, currently engaged in putting a year course in high school chemistry on 160 films for the Encyclopaedia Britannica Corporation, and from Howard E. Norris, Academic Director of the Loomis Institute, with reference to the Pre-College Science Center supported at Loomis Institute by the Dorr Foundation.

With this resource material as a background, the conference members were then asked to organize themselves into work groups in accordance with their interests. Three groups were set up including Group A dealing with bonding as the central theme for a high school chemistry course, Group B which was made up of those desiring to consider other possible central themes, and Group C which was concerned with a program in chemistry which might be correlated with the efforts of the Physical Science Study Committee. The following summary presents the conclusions from reports of the three groups which were the consensus of the conference.

Group B. The group decided to start with a definition of what chemistry teaches and accepted as suitable (but not exclusive of other ways of defining chemistry) the following statement worked out by Professor Anna Harrison of Mt. Holyoke and her students:

Chemistry deals with:
- What substances react
- The conditions under which they react
- What products are formed
- The energy changes involved
- The state of equilibrium attained
- The rates at which reactions occur
- Generalizations from the above
- Theories which explain the above.

Any chemistry course should:

Give the student personal experiences during which he would participate in scientific activities;

Be rooted as far as possible in the life of the student, in that physical activities and perceptions (e.g., experiments) should at least start with familiar things. The course should also feed the life of the mind; it must not be authoritarian and it must show how to go about solving problems.

Be flexible in terms of *content*, so that the teacher can teach what he is excited about and interested in. It should also be flexible in level of approach so as to be applicable to bright and to slow students, and flexible in terms of presentation so that experiment, books, television, etc., can be used as the exigencies of the situation (i.e., equipment of the school) demand.

Illustrate, with emphasis by the teacher, that what we are trying to teach is a dynamic process in which learning, discovery, generalization, etc., feed back to produce better learning, discovery, and generalization. It should be emphasized that this is a continuous process and that it teaches problem solving.

This group, in its progress reports, included a sample beginning of a course in order to show how, starting

[1] *See* J. CHEM. EDUC., **35**, 54 (1958).
[2] *See* J. CHEM. EDUC., **35**, 56 (1958).

with "selected bits of chaos" ("reality") and attempting to bring order out of this by the use of reason and imagination, the student can be taught chemistry. The group felt this approach, formalized in this way, emphasized the difference between the authoritarian training method which starts with a conclusion, and the flexible, empirical, *educational* method which begins with experiences. They emphasized that much of this represents what is actually attempted now, and thus the program can start with present situations and gradually improve them; that it is pragmatic and empirical, and that particularly through the *explicit* operation of "feedback" it allows for the continual correction of errors.

The difficulties of taking such an approach as this were discussed by the full conference—particularly with respect to college entrance examinations. It was felt that although these difficulties might in time be surmounted, it might not be practical to conduct an *entire* course along these lines. However, it was agreed that the course should be *begun* on these lines, especially since this kind of beginning gives the student some early successes which are deeply satisfying to him.

Group C emphasized that there is more than one way to attack the teaching of chemistry. A definition, not at odds with that first given, but more related to the Group C report was that chemistry deals with number, geometry, and motion (Hinshelwood). Group C felt that *the best and most fruitful kind of course would integrate (in a two year program) chemistry and physics.* That this is already done in some schools, that it is particularly feasible in a school with only one science teacher, and that it does introduce administrative (scheduling) difficulties in a large school with specialist-licensed teachers were all recognized. However, the need for the statement of ideals by this conference was stressed; and it was therefore agreed that experiments with these ideas should be pressed in many relatively small-scale applications, some of which might operate under a Group B type of procedure.

Group A had been primarily concerned with further amplification of the valence-bond central theme as discussed at the Reed College Conference.[2] An expanded outline and some suggestions for bibliographies and for illustrative experiments and demonstrations were worked out. However, it should be emphasized that these suggestions are still tentative in nature and need further careful consideration.

The contributions of Group A were found to be consistent with the general ideas previously presented from the other two discussion groups in that a program based on the valence-bond theme could be utilized as part of the integrated physics-chemistry approach of Group C, and in addition this program could also be taught in consonance with the Group B scheme which would contribute to it the continual emphasis that generalizations of theories must arise out of data. It was the opinion of some members of the conference that it may be dangerous to define a full course in chemistry in terms only of the chemical bond; that in any case clear distinctions should be made between molecular bonds and intermolecular interactions; and that every effort should be made to keep clear the distinctions between theory and data. With these provisos, it was agreed that the valence-bond approach might very fruitfully make up a large part of a course when taught by one who believes in this method and is enthusiastic about it.

Resolutions Adopted

(1) Since neither modern chemistry nor physics can be understood without a knowledge of the other science, we believe that the most effective means of teaching these subjects in high school is through an integrated two year course in the two sciences. If the current separation of courses in physics and chemistry is to be continued, attempts should be made to develop new approaches to the teaching of chemistry which take into consideration the importance of basic physical principles in the development of modern chemistry. To obtain the maximum advantage from these changes, the subsequent college science courses must be revised to be consistent with any new high school program.

After examination of the approaches to course content improvement taken by the mathematicians and physicists, *we believe that the design of any program should be initiated through study and trial by three or four independent groups.* These should operate under the direction of a central steering committee. This would permit the evaluation of each different approach in terms of the content of high school science and the circumstances in which the courses are offered. We believe that this approach would be particularly fruitful in developing the ultimate direction of a large scale attack on the problem. It should be understood that, once developed, the whole program should be subject to periodic revision.

We believe the composition of all the groups involved in this program should include people who will be responsible for the teaching and successful implementation of the high school and college science program, as well as those who can contribute to its orientation because of their involvement in the development of scientific thought. The ultimate success of the program will demand genuine cooperation among all personnel involved.

(2) The Wesleyan Chemistry Conference members are vitally concerned with the proper instruction of the children in high school science. The most effective science teaching requires laboratory work by pupils and extensive demonstrations by both students and teachers; this kind of program requires time and thought.

To make more effective use of these teachers we recommend that science teachers be provided with adequate time during the school day for the preparation of laboratories, demonstrations, and the supervision of students science projects.

(3) Since the Strong-Wilson central theme approach is the one of several possible programs which this group now has ready for trial, we wish to encourage its use on an experimental basis in as many high schools as possible during 1958–59. We also believe that these experiments should be evaluated in a working conference during the summer of 1959. If at that time the "chemical bond" central theme approach proves to have been successful, we believe that work should be done by those attending the conference on a textbook, and on laboratory and lecture experiments to be used in further experimentation with this course.

(4) It was moved, seconded, and passed that encouragement be given to interested persons and groups to develop a course based on the report of Group B.

The members of the conference wish to acknowledge their debt to the National Science Foundation for financing the Wesleyan Conference and to express to the Foundation their gratitude for the privilege of being able to attend this meeting of high school and college teachers who have a deep concern for the improvement of chemical education in the secondary school.

As a postscript to the above report it should be noted that Reed College has submitted a proposal to the National Science Foundation for the summer of 1959 to accomplish the objectives described in resolution 3 and this proposal has been accepted. In addition, the members of Group A intend to issue six Newsletters during the academic year 1958–59 to members of the group and others who are interested. This is a device for reviewing programs set up in high schools in which chemical bonding will be considered as a theme and for maintaining a thread of continuity in preparation for the 1959 Reed Conference.

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History of the Pacific Southwest Association of Chemistry Teachers

On the occasion of the 115th meeting of the American Chemical Society in San Francisco, in the spring of 1949, the vision of a dedicated, dynamic professor from an Oklahoma college came true. Otto M. Smith, then chairman of the Committee on College Teaching of the Division of Chemical Education, had written innumerable letters to teachers in the Western States, suggesting the formation of an organization of college chemistry teachers. On the afternoon of March 29, 1949, as scheduled in the Divisional program, Otto Smith met with over one hundred representatives of the teaching profession from California, Oregon, Washington, and Idaho.[1] Because of the vast distances involved, the meeting soon split into two groups. The Pacific Northwest group elected A. H. Kunz as its chairman. The California group elected L. Reed Brantley chairman, and Valerie Phillips secretary, until a constitution clarifying the purpose, scope, and activities of the group could be prepared. At a special committee meeting called the next evening by Dr. Smith, it was suggested that membership be restricted to college teachers of chemistry and that joint meetings of the Northwest and Southwest Associations be held in San Francisco every second year, to take advantage of the facilities and services of the Pacific Chemical Exposition. It was also suggested that the support of the American Chemical Society be enlisted through affiliation with the Division of Chemical Education.

For the next few months there was a bustle of activity in the Los Angeles area. Matters of policy and goals were clarified to permit the preparation of a constitution for consideration by the Association, and a set of bylaws for the Southern Section. The constitution of the Association was approved at the first Annual Meeting, held in conjunction with the Pacific Chemical Exposition in San Francisco, November 4–5, 1949, scarcely six months after the first informal gathering. Over 150 teachers from 40 educational institutions attended the two-day program at which Arthur Furst was elected the first president of the Association.

Organizational Structure

The Association was divided into local sections for administrative reasons and to provide local programs. Chairmen of the local sections were to serve as vice presidents of the Association. Other population centers in California, as well as in Arizona, Nevada, and Utah, were to be invited to form local sections. The stated purpose of the Association was to encourage the development and improvement of chemistry instruction at the college level and to consider problems arising relative to the teaching of chemistry. The membership dues included a subscription to the JOURNAL OF CHEMICAL EDUCATION, which became the official organ of the Association, with a section entitled Proceedings of PSACT, for inclusion each month of official business and news of the Association and selected articles. This fortunate arrangement was made possible on a basis similar to that of the New England Association of Chemistry Teachers. G. Ross Robertson was appointed Editor for the Association and an Associate Editor of THIS JOURNAL. A press release enthusiastically stated that membership was open to anyone living in Arizona, California, Nevada, New Mexico, and Utah, who was actively participating in a college teaching program or who had an interest in the field. On the other hand, by the end of the first year, Dr. Kunz reported that after further investigations, it had seemed unwise to continue the organization of the Pacific Northwest Association of Chemistry Teachers because of the multitude of scientific and educational organizations already active in that area.

Affiliations

A careful investigation of the possibility of affiliation of PSACT with the Division of Chemical Education disclosed that this was not practical, since ACS regulations made it necessary for all members of an affiliated group, such as PSACT, to hold membership in the ACS as well. Cooperation with the Division continued through the privileges afforded by the JOURNAL OF CHEMICAL EDUCATION, while cooperation with the local sections of the ACS took the form of traditional sponsorship of chemical education programs at Divisional and Regional meetings. PSACT became an associated society of the American Association for the Advancement of Science in 1950, and an affiliated society in 1956. After such knotty problems had been settled, the Association was off to a good start and in the words of Dr. Furst, "The question of improving instruction in chemistry at all levels, just like the weather, is constantly being discussed. The newly organized PSACT is going to try to do something about it."

The variety of programs presented at the local level is illustrated by a panel discussion held by the Southern Section on what to take out of freshman chemistry, followed by an address by Linus Pauling on what should

Presented as part of the Symposium on the History of Chemistry in California before the Division of History of Chemistry at the 133d Meeting of the American Chemical Society, San Francisco, April, 1958.

[1] J. CHEM. EDUC., **27**, 166, 576 (1950).

be put back. The Northern Section, not to be outdone by the Southern group's first annual joint program with the Southern California Regional ACS meeting, held a joint session with the National Science Teachers Association on, "Seconday School Science in the Modern Curriculum." This was in April, 1950, seven years ahead of the times and "Sputnik I." By the time the second Annual Meeting of the Association was held on November 3–4, 1950, at the California Institute of Technology and Occidental College, the membership of the two sections was well over one hundred and was increasing rapidly.[2]

Formative Years

During the next few years, PSACT continued its healthy growth, turning its attention to the discussion of the content and purpose of college courses in general chemistry and analytical chemistry, discussion of the place of organic chemistry in the junior college curriculum, and the problem of transfer of credit to the universities.[3] These topics, combined with such varied programs as recent advances in radiochemistry, atomic energy, chromotography, microanalysis, and the use of microcards in chemistry libraries, sustained interest at a high level. The third Annual Meeting of PSACT was held in San Francisco, November 2–3, 1951, and was concerned with the discussion of more effective science teaching in our colleges. L. Reed Brantley was elected president. In December, 1951, the first *PSACT News Letter* was distributed to its members by the editor, Robert Isensee. Also, the first *Membership Directory* was published by the Association secretary, Blanche Bobbitt. The membership numbered 145, including thirteen high school chemistry teachers, all from the Southern Section, a chemistry textbook publisher, and several research chemists in industry. An enthusiastic group of teachers with the natural desire to talk shop, combined with leadership which took advantage of the assistance of well-established societies with related interests, had smoothed the way over the first few critical years of the new organization.

Expanded Activities

During the next three years, PSACT provided thought-provoking panel discussions on subjects such as the screening and selection of students for freshman chemistry courses to reduce the high percentage of casualties of the first year. In 1952, with Murray Clark as president, many varied programs were provided. These included speakers of the caliber of Glenn T. Seaborg, luncheon meetings with a new twist of seating members at the tables for shop talk according to their choice of subject matter, high level talks about graduate chemistry programs with the inevitable discussion of the desire of some for doctor's degree programs in chemistry designed for the needs of chemistry teachers, and vital information on radiological hazards in the recycling of fission products in the biotic cycle. In 1953, the sponsorship of the Southern California Science Fair by PSACT was begun. During 1954, with Howard Benninghoff as president of what had become known as the State Association, the design of new chemistry buildings to provide for increasing enrollments and modern teaching methods, were popular topics for group discussion.

Changes in the thinking of the group with the times were reflected at the sixth Annual Meeting, held December 29, 1954, in cooperation with the Annual Meeting of the AAAS at the University of California, Berkeley.[4] Serious consideration was given to means of bringing the two sections of the Association closer together to produce a more unified and stronger group. It was suggested that with further growth, PSACT might well add a Central Section, or that a more central meeting place between San Francisco and Los Angeles be tried. The growth in membership brought up the consideration of actively inviting high school teachers who were interested in chemistry to join the Northern Section as was the practice in the Southern Section. The viewpoint was advanced that the subscriptions to the JOURNAL OF CHEMICAL EDUCATION, included in dues, might serve as a financial barrier to an increase in high school teacher membership.

The retirement of G. Ross Robertson from teaching ended his valuable service as PSACT representative and Associate Editor of the JOURNAL OF CHEMICAL EDUCATION. Fortunately, with the appointment of John L. Abernethy to replace Dr. Robertson, the publication of PSACT Proceedings has continued uninterrupted.[5]

A Challenge

With the development of world events of the last few years, science teacher associations such as PSACT have been challenged to assume added responsibilities. Under the able leadership of PSACT officers of both the Association and the locals sections, plans have been considered for chemistry workshops, summer employment for chemistry teachers, and a new emphasis on the problems and needs of high school chemistry teachers. The trend of public interest in the gifted high school science student has called attention to the need for closer cooperation between high school and college chemistry teachers to consider motivation and training of superior high school chemistry students. PSACT has drawn heavily upon its members among the high school teachers and administrators for advice and leadership in these new activities.

Yet after ten years of activities and healthy growth, there are still a few basic problems to be solved. One of these is better communication between the officers of the two sections and those of the State Association. After a lapse of two years, a 1958 directory listing nearly 300 members has been published by the secretary, Dorothy Craig. Another related problem is the need for a unified activity program for the two sections through the medium of the Association.

The future of PSACT will constitute a challenge to its officers for some years to come. Whether public sentiment and the urgencies of the period can be used to strengthen and extend the scope and purpose of the Association to include greater participation in the problems of the teaching of chemistry at all levels, and the training of the much needed scientists of the future, remains to be seen.

[2] J. CHEM. EDUC. **28**, 48 (1951).
[3] J. CHEM. EDUC., **28**, 224, 606 (1951).
[4] J. CHEM. EDUC., **32**, 284 (1955).
[5] ABERNETHY, J. L., J. CHEM. EDUC., **33**, 182 (1956).

Officers of the Pacific Southwest Association of Chemistry Teachers

1949: Temporary chairman, L. Reed Brantley, Occidental College. Temporary secretary, Valerie Phillips, San Francisco College for Women.

1950: President, Arthur Furst, University of San Francisco. Vice presidents: Benjamin Naylor, San Jose State College; L. Reed Brantley, Occidental College; H. Murray Clark, San Jose State College; Robert Harper, Los Angeles City College. Secretary, Valerie Phillips, San Francisco College for Women. Treasurer, Claude Merzbacher, San Diego State College.

1951: President, L. Reed Brantley, Occidental College. Vice presidents: Harry Redeker, San Mateo College; Philip Gill, Glendale College. Secretary, Blanche Bobbitt, Los Angeles City Schools. Treasurer, Richard Wistar, Mills College.

1952: President, H. Murray Clark, San Jose State College. Vice presidents: Howard Benninghoff, City College of San Francisco; Frank L. Lambert, Occidental College. Secretary, Gertrude Cavins, San Jose State College. Treasurer, Ernest Bickerdike, UC-Santa Barbara.

1953: President, Ernest Bickerdike, UC-Santa Barbara. Vice presidents: E. B. Womack, Fresno State College; W. Roy Newsom, Whittier College. Secretary, Lionel Joseph, San Diego State College. Treasurer, T. Bentley Edwards, Chico State College.

1954: President, Howard Benninghoff, City College of San Francisco. Vice presidents: Manfred Mueller, City College of San Francisco; Harper Frantz, Pasadena City College. Secretary, Mother Agnes Schmit, San Francisco College for Women. Treasurer, Sister Agnes Ann, Immaculate Heart College.

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Report of the New England Association of Chemistry Teachers

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Chemistry in Sanitary Engineering

Sanitary engineering is a phase of applied science which is devoted solely to improving the living conditions of humans. This is a continuation of an effort which has been in progress for ages, particularly against the Third Horseman of the Apocalypse, disease. Originally much of the effort was based upon superstition, seasoned with some sound practices developed from interpretations of natural phenomena made by unusually keen observers. It was not until the science of chemistry was developed that man began to battle with the enemies in his environment with any real degree of success. The development of the science of bacteriology about 1870 provided the "trump card" which enabled sanitary chemists and others concerned with the public health to make marked progress in stamping out and controlling the vectors of disease transmission.

The solution of any sanitary engineering problem requires that it be defined both qualitatively and quantitatively. This usually requires that much analytical data be obtained before design and construction of treatment units can commence. Furthermore, successful operation of most sanitary engineering facilities demands close control employing analytical procedures. Analytical chemists, with an occasional assist from other scientists and engineers, have provided methods for the analysis of practically any material with which the sanitary engineer has to deal. Most of the procedures have had to be developed for use in dilute solutions, i.e., for measurement of milligram and microgram amounts. The results of these efforts are published in "Standard Methods for the Examination of Water, Sewage and Industrial Wastes" (*1*), and revised editions are issued from time to time. "Standard Methods" undoubtedly, represents the most important contribution of the chemist to the sanitary engineering profession.

Water

The chemist has played three important roles in the area of water supply problems. First, his analytical procedures have served as the basis for establishing many of the water quality criteria. Second, he has developed water purification processes to upgrade waters and make them acceptable for any particular use. Third, the sanitary engineer often has the alternative of developing one of two or more supplies for a given use. The analytical data obtained by the chemist usually provide the information needed to determine which supply will provide the most satisfactory water from the viewpoints of acceptability and economics.

Hygienic. It was not until the Broad Street Pump incident in the London cholera epidemic of 1854 (*2*) that strong circumstantial evidence was developed to associate the spread of cholera with a water supply. The science of bacteriology was yet unborn and it was not until 1892, at the time of the great cholera epidemic in Hamburg, Germany (2), that conclusive proof of the association was obtained.

Investigations of the Broad Street Pump incident in London had proved that the well water had become contaminated with sewage. This gave chemists a clue to be followed since the chemical differences between water and sewage are quite large. Most natural waters have relatively low concentrations of ammonia and organic nitrogen and some have low chlorides. Sewage, on the other hand, is rich in these substances. For these reasons, analyses for nitrogen in its various forms and for chlorides became standard tests for evaluating the hygienic quality of water.

Following the development of the science of bacteriology, a great deal of effort was made to ascertain the hygienic quality of water through tests for cholera and typhoid organisms. It soon became apparent that isolation and enumeration of these specific organisms was too difficult. It was noted that sewage contaminated waters were always rich in certain other organisms which were not common to natural waters. These became known as colon group organisms because of their natural habitat in the intestine of man and warm-blooded animals. Tests for the enumeration and isolation of the colon group of organisms were developed about 1900 and, at the present time, are so well refined that chemical tests are seldom needed to judge the hygienic quality of water. However, chemical tests did provide the major basis of judgment for nearly one-half of a century.

Toxicological. Natural waters seldom, if ever, contain materials which cause violent or chronic illness which results in death. Promiscuous discharge of industrial wastes, as has occurred in some areas, contaminates both ground and surface waters. Some contaminants become segregated by natural processes but others do not. Cadmium and cyanides are examples of particularly toxic ions for which humans have very low tolerance levels. Chemical tests are required to detect their presence and the concentrations involved.

Presented at the 20th Summer Conference of the New England Association of Chemistry Teachers, University of Rhode Island, Kingston, August 21, 1958.

Nitrates are normally present in surface waters in relatively small amounts but may occur in ground waters in amounts up to a few hundred milligrams per liter. Such amounts are of no concern to small children or adults but it has been shown that concentrations of nitrates in excess of 80 milligrams per liter may be toxic to formula-fed infants. The nitrates themselves are not toxic but are the source of the toxic material. In some manner the nitrates are reduced to nitrites which combine with the red corpuscles of the blood to produce a complex which is incapable of carrying oxygen. This gives rise to a condition known as Methemoglobinemia or "blue baby" and, unless relief is obtained, the infant will die for lack of oxygen. For this reason, the nitrate content of water is an important consideration.

Physiological. Some natural waters contain dissolved salts or combinations of dissolved salts which may have an effect upon body function but do not result in a fatal condition. Waters with high salt content often produce constipation in people not accustomed to them. Others that contain appreciable amounts of magnesium and sulfate may cause a diarrhetic condition. Some waters contain amounts of fluorides large enough to produce a condition known as mottled enamel in teeth. Chemists have developed methods for removing fluorides to safe levels. A certain amount of fluoride is needed for the development of normal teeth. This has led to the practice of supplementing water supplies deficient in fluoride to an optimum level of one milligram per liter. In places where supplementation is practiced, the chemist has a real responsibility in providing accurate data so that the program may be effectively administered.

Taste and Odor. Taste and odor problems may arise from natural causes or they may be the result of some contaminating material which has gained access to the water through discharge of sewage or industrial wastes. Ground waters are usually relatively free of taste and odor. They sometimes contain hydrogen sulfide, however. The chemist's knowledge of ionization constants, Henry's law, and oxidation procedures is called on to develop a process for removal.

Many surface waters support extensive growths of aquatic organisms which give rise to taste and odor problems. Certain species of algae and protozoa are notorious. A great deal of misinformation has persisted in some areas concerning the factors which influence the biological productivity of surface waters. The chemist, employing principles developed long ago by agricultural chemists, has shown that biological productivity is a function of the amount of fertilizing materials entering the body of water as modified by Liebig's Law of the Minimum (*3*).

Odor problems have become more and more severe in many water supplies over the past one or two decades. The Ohio River and Lake Michigan in the Chicago area are notable examples. Pollution by industrial wastes had long been suspected as the cause, but direct evidence was difficult to obtain because procedures for isolation and identification of the trace amounts involved, except for phenol, had not been developed. As a result, taste and odors were characterized by descriptive terms such as "musty," "marshy," "geranium," "cucumber," "pig-pen," etc. Within the past few years a major break-through has occurred in resolving taste and odor problems on a scientific basis. Chemists and engineers at the Robert A. Taft Sanitary Engineering Center in Cincinnati have used activated carbon filters to concentrate the trace materials (*4*). Elution of the activated carbon has provided extracts containing sufficient amounts of materials for separation into acidic, alkaline, and neutral fractions for further isolation and characterization. Analysis by infrared spectrometry has provided a great deal of specific information.

Irrigation Waters. In the western part of the United States much of the agricultural economy depends upon the use of irrigation water, and in other parts of the country supplemental irrigation is becoming quite popular. The chemical composition of water used for irrigation purposes is of importance from two viewpoints. First, it must not contain elements which are injurious to the particular crop. Boron is a notable example. Its concentration must be kept below 0.3-1.0 mg/l to prevent injury to sensitive crops such as citrus and other fruits, nuts and beans. Second, the sodium content of waters, or more properly the sodium-alkaline earth ratio, must be kept within certain limits to maintain proper soil structure. This is particularly true in arid areas where salts accumulate in the soil through lack of purging or leaching by occasional heavy rainfall. Chemists, particularly those at the U.S. Salinity Laboratory, Riverside, California, have contributed greatly to water quality requirements for irrigation waters (*5*).

Water Purification

Coagulation. Many cities, particularly the larger ones, are dependent upon surface water supplies. A few like Boston, New York, and Seattle are fortunate enough to have supplies which do not require clarification before use. The majority do, however. Surface waters may contain a wide variety of suspended matter ranging from organic substances contributed by domestic sewage, industrial wastes, or soil washings to mainly inorganic matter originating from soil erosion, mining, and industrial operations. In the main these materials are colloidal in nature and application of the fundamentals of colloid chemistry are essential to their removal. In this connection, a knowledge of the Schulze-Hardy rule and the concepts of mutual coagulation, by oppositely charged colloids, is basic.

Softening. All natural waters contain dissolved salts as impurities depending upon the nature of the soil with which the water has been in contact. Solution of appreciable amounts of calcium, magnesium, and strontium salts produces waters which are commonly termed "hard." "Hardness" is usually related to the soap-consuming capacity of the water. Removal of the offending ions obviously is a chemical problem, accomplished by precipitation or ion-exchange methods.

Demineralization. Many industries require large amounts of water which is of "distilled quality." Such supplies were obtained formerly by expensive distillation methods. Today much water of low solids content is produced by use of a combination of resins, one which is capable of exchanging hydrogen ions for metallic ions and the other which combines with the

free acids that are formed allowing a water to flow from the units which is comparable to distilled water.

Some industries require water that has special characteristics. Notable are the brewing and power industries. Demineralization of the local water allows production of a water of any desired composition by adding salts to the demineralized water. This factor has enabled the brewing industry to locate its plants in any geographical location and maintain a uniform product.

Disinfection. The production of hygienically safe water is dependent upon the use of some agent which will destroy all pathogenic and parasitic organisms which may be present in the raw or chemically treated water. Chlorine, or its compounds, is the popular choice of disinfecting agent in the United States. Its use was enhanced by the development of a simple chemical test employing orthotolidine for measuring the chlorine remaining in the water (residual chlorine) after the desired contact time.

For many years chlorination of public waters was controlled by the simple orthotolidine test. Gradually, however, it became recognized that the disinfecting power of chlorine varied considerably. Research soon established that orthotolidine measured chlorine in the form of chloramines as well as free chlorine. Subsequent studies showed that chloramines were much weaker in disinfecting power than free chlorine residuals and that chloramines were the dominant form of residual at the usual *p*H of natural waters unless chlorine was added in excess of the combining power of the ammonia present. After sufficient chlorine had been

$$NH_3 + Cl_2 \rightarrow NH_2Cl + HCl$$
$$NH_2Cl + Cl_2 \rightarrow NHCl_2 + HCl$$
$$NHCl_2 + Cl_2 \rightarrow NCl_3 + HCl$$

added to convert all of the ammonia to nitrogen trichloride, the chlorine was free to react with water to establish the normal equilibrium:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

This knowledge, provided largely by chemists, required that analytical methods be developed for differentiation of chloramine and free chlorine residuals.

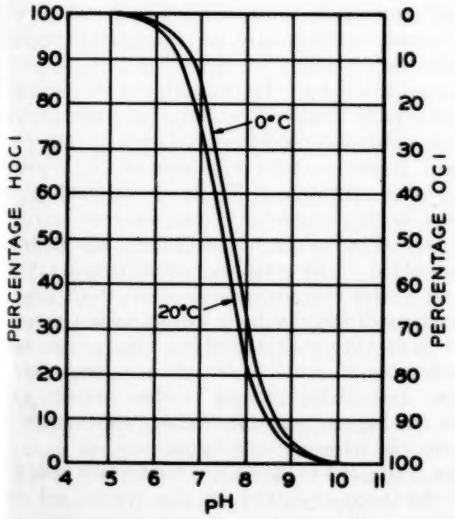

Figure 1. Relative amounts of HOCl and OCl^- present at various *p*H levels.

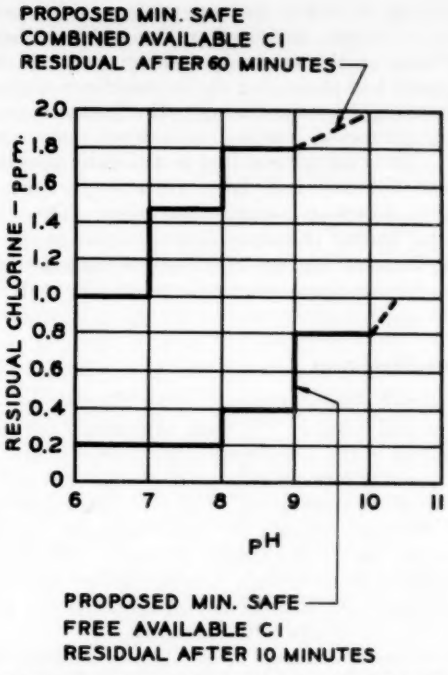

Figure 2. Recommended chlorine residuals at various *p*H levels.

With the advent of disinfection with free chlorine residuals, it soon became apparent that the killing power was a function of *p*H. It was noted that the disinfecting power decreased as the *p*H increased. The solution to this enigma was produced by Fair, *et al.* (*6*). They showed (Fig. 1) the quantitative relationships between undissociated hypochlorous acid and hypochlorite ion over the *p*H range of interest in waterworks practice. From this information it has become recognized that hypochlorous acid is a more potent disinfecting agent than hypochlorite ion, and that *p*H is a factor to be recognized in disinfection practice. Subsequent studies on the effect of *p*H on the disinfecting power of chloramines have shown them to be somewhat less effective at the higher *p*H levels. The recommended modern practice for disinfection by combined or free chlorine residuals is summarized in Figure 2.

For many years, considerable controversy has occurred over the relative disinfecting power of chlorine versus hypochlorites. The chemical answer is that hypochlorous acid results from the hydrolysis of each and its potency is a function of the *p*H. Chlorine tends to reduce the *p*H while hypochlorites tend to increase the *p*H. In poorly buffered waters the *p*H change can be considerable while in strongly buffered waters the change is negligible for the dosages normally employed.

Corrosion Control. The sanitary engineer's responsibilities are not finished when he has provided a satisfactory water supply. He must also provide for a distribution system to carry the water to the point of use. This is a giant network of pipes which vary greatly in size and must carry water under considerable pressure. Cast iron and steel have been the favorite ma-

terials and, of course, both are subject to the corrosive action of oxygen dissolved in the water. Chemists' knowledge of the solubility product principle led to the practice of protecting the iron surfaces of pipes by conditioning the water through *p*H adjustment to cause a thin protective coating of calcium carbonate to form. This practice was first proposed by the German chemist Tillmans and, later, refinements were made by the American chemist Langelier. The electrochemical theory of corrosion serves also as the basis of corrosion prevention by means of cathodic protection, a system commonly employed on elevated storage tanks.

Sewage Treatment

Activated Sludge Process. Two English chemists, Ardern and Lockett (*7*), were responsible for the development of the activated sludge process which is the most popular form of sewage treatment in use today, particularly in large cities. Like all biological processes, it is affected seriously by environmental factors as well as the nature and amount of food. Chemists have contributed much toward a better knowledge of: air requirements (*8*), nutritional requirements (*9*), growth rates (*9*), and effects of temperature (*10*).

Considerable volumes of air must be supplied in the activated sludge process. Its purpose is twofold: to maintain aerobic conditions and to keep the activated sludge in suspension and distributed throughout the mass of liquid under treatment. In recent years a great deal of trouble has been encountered with frothing or foaming of the aeration tanks. This difficulty has been associated with the shift from the use of soaps for domestic cleansing to synthetic detergents. Research has established that synthetic detergents differ greatly in their biological assimilability (*11*). Some, particularly the alkyl benzene sulfonates derived from propylene which are so popular in compounding heavy-duty products, are extremely resistant to biological oxidation. The surfactants which remain after other organic pollutants have been destroyed are considered to be the major cause of frothing. There is considerable pressure upon detergent manufacturers in the United States and England to substitute biologically "soft" for biologically "hard" surfactants in their formulations. In the meantime, antifoaming agents and spray systems are being used to keep frothing under control.

Anaerobic Sludge Digestion. Strange as it may seem, much of the knowledge concerning the mechanism of the anaerobic degradation of organic matter by mixed populations of organisms has been developed by chemists. Most of this can be credited to A. M. Buswell and his colleagues (*12*) of the Illinois State Water Survey. In addition, he has added considerable information relative to the methane-forming bacteria and their substrate requirements.

In the anaerobic degradation of crude organic matter, such as sewage sludge, by a mixed population of bacteria native to domestic sewage, saprophytic organisms hydrolyze and oxidize the organic matter to produce a series of simple compounds of which the low molecular weight fatty acids (mainly acetic) are a major endproduct. The methane formers convert the simple endproducts to methane and carbon dioxide. In case the methane formers are incapable of utilizing the endproducts formed by the saprophytic bacteria as fast as they are formed, an accumulation will occur which may cause drastic decreases in *p*H with ultimate failure of the process. This knowledge led to the development of the volatile acids test for controlling sludge digestion and, undoubtedly, is the most important contribution of chemists to the practice of sludge digestion.

Sludge Filtration. Sewage sludges, both raw and digested, have extremely poor filtering characteristics and some form of filter aid is required to make filtration economical. Lime and ferric chloride are the chemicals most commonly used for conditioning of sludge. Since vacuum filtration is a unit operation in chemical engineering practice, it was natural that chemical engineers became interested in the conditioning of sewage sludge. We are indebted to A. L. Genter (*13*) for most of our present-day concepts. The ferric salts are considered to be effective in coagulation of colloidal substances and in causing the release of bound water. The addition of lime results in the precipitation of calcium carbonate which provides inorganic matter that serves as a filter aid.

All sludges contain buffering materials which tend to hold the *p*H at a given level. Digested sludge is particularly well buffered with bicarbonates, and appreciable amounts of ferric salts are required to lower the *p*H for effective coagulation of the colloidal solids. The ferric salts required to destroy the buffer are precipitated as ferric hydroxide of gelatinous character which increases the filter aid requirements materially. Genter (*14*) introduced the practice of washing digested sludges (elutriation) to decrease the buffering capacity, thereby reducing the ferric salt and lime requirements. This is an excellent example of how chemical knowledge has been used to decrease the costs of waste treatment.

Industrial Waste Treatment

In the field of industrial waste treatment, chemists and chemical engineers have worked in close alliance to find solutions to a wide variety of problems. Industrial wastes vary greatly in character from industry to industry.

Inorganic Wastes. The majority of the wastes which are principally inorganic in character originate from the mining and metal processing industries. The most important liquid wastes result from pickling, anodizing, and plating operations. Wastes from pickling contain mineral acids and metallic ions such as iron, copper, and zinc, all of which can be effectively removed by precipitation as hydroxides. Anodizing and chrome-plating wastes contain chromic acid which may be recovered profitably by basic resins under some conditions. Oftentimes reduction to chromic ion and precipitation as chromic hydroxide is more economical. Copper and nickel plating wastes contain cyanides which are highly toxic and must be destroyed before they may be released to receiving streams.

The treatment of inorganic wastes has been a "natural" for people trained in the specialized area of chemistry. Precipitation of metallic hydroxides and reduction of chromates was easy, but the destruction

of cyanides was more difficult. For a long time, the favored method was treatment with sulfuric acid to release HCN, with dispersal of the obnoxious gas through tall stacks. This was far from a perfect system because of pollution of the atmosphere. Eventually, chemists developed an oxidation method employing chlorine under controlled *p*H conditions. The oxidation may be controlled to produce relatively nontoxic cyanates or it may be caused to go to completion with oxidation of cyanide to carbon dioxide and nitrogen at *p*H levels above 8.5, according to the following equations:

$$CN^- + 2\,OH^- + Cl_2 \rightarrow CNO^- + 2Cl^- + H_2O \text{ (rapid)}$$
$$2CNO^- + 4\,OH^- + 3Cl_2 \rightarrow 2CO_2 + N_2 + 6Cl^- + 2H_2O \text{ (slow)}$$

The oxidation can be stopped at the cyanate stage by controlling the chlorine dosage because of the speed of the first reaction as compared to the second. Total oxidation can be controlled by conventional oxidation-reduction potential equipment.

Organic Wastes. Most other industrial wastes contain organic matter in sufficient amounts to require biological treatment for purification. In general, trickling filters and the activated sludge processes have been used. A few wastes of high pollutional strength are treated directly by anaerobic digestion. Because of the wide variety and character of wastes requiring treatment, a great deal of care and ingenuity has had to be exercised in providing treatment facilities. On the other hand, the challenge offered by the unusual character of some industrial wastes has allowed experimentation under conditions which have led to a broadening of the concepts of biological treatment (*15*).

For a long time it was considered that biological treatment of liquid wastes required pre-neutralization into a *p*H range of 7 to 8. Studies have shown that acid wastes must be neutralized to such an extent that all mineral acids are satisfied, but whether the *p*H must be raised above 5 depends upon the character of the waste and the manner in which the waste is fed to the biological unit.

Alkaline wastes with *p*H levels as high as 11.5 have been satisfactorily treated by the activated sludge process with considerable savings of acid. This new knowledge is based upon the fact that carbon dioxide is released during biological oxidation of organic matter:

$$\text{Organic matter} + O_2 \xrightarrow{\text{Bact.}} CO_2 + H_2O$$

If the *p*H of the system is below 8.5, the carbon dioxide is lost to the atmosphere. However, if alkaline wastes are added to keep the system at about *p*H 9, the carbon dioxide is used to neutralize the incoming waste of high *p*H. Studies have shown that the bacteria responsible for oxidizing the organic matter readily adapt themselves to *p*H levels as high as 9 without serious loss of efficiency.

Biological processes of waste treatment involve the use of microorganisms which have nutritional requirements akin to those of higher forms of life with one exception. Bacteria, for example, are capable of synthesizing protein from ammonia and organic sources of carbon. Therefore, it is not necessary to provide protein as food. Activated sludge grown on a diet with adequate amounts of nutrients has an empirical formula which approximates $C_{118}H_{170}O_{51}N_{17}P$. In order for each species of organism to maintain itself generation after generation, both nitrogen and phosphorus must be present. Sulfur is another element of importance but, since most water supplies contain sulfates, most wastes contain an abundance of available sulfur.

Many industrial wastes contain organic matter such as carbohydrates, alcohols, esters, and acids which are deficient in both nitrogen and phosphorus. Supplementation with nitrogen and phosphorus is often required to provide the necessary "bricks and mortar" for the production of normal daughter cells. The soil chemist speaks of proper carbon to nitrogen ratios. The sanitary engineer does not normally measure carbon but determines its equivalent in terms of biochemical oxygen demand (B.O.D.). Investigations have shown that a ratio of B.O.D. to N to P of about 100:5:1 must be maintained to maintain an activated sludge with a composition shown above. Deficiencies in either nitrogen or phosphorus will result in the production of a sludge with a smaller percentage of the limiting element. The sludge produced under such conditions is usually less efficient and has other undesirable properties.

A number of industrial wastes contain materials which are toxic to microorganisms when present in sufficient amounts. Two of particular interest are phenol and formaldehyde. Laboratory and plant scale studies have shown that certain species of bacteria thrive on these organic materials, and activated sludges can be developed from wastes containing as much as 1500 mg/l (0.15%) of either one. This information has led to the concept of toxicity thresholds and has taken much of the fear of toxicity away from industrial wastes, since most situations can be solved by dilution of the waste to levels below the toxicity threshold.

Literature Cited

(1) "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes," 10th ed., Am. Pub. Health Assoc., New York, **1956**.
(2) Rosenau, M. J., "Preventive Medicine and Hygiene," 6th ed., Appleton-Century-Crofts, Inc., New York, **1935**.
(3) Browne, C. A., "Liebig and the Law of the Minimum," Publication No. 16, Am. Assoc. Advancement of Sci., Washington, D. C., **1942**.
(4) Middleton, F. M., Braus, H., and Ruchhoft, C. C., *J. Am. Water Works Assoc.*, **44**, 538 (1952).
(5) Wilcox, L. V., *ibid.*, **50**, 650 (1958).
(6) Fair, G. M., Morris, J. C., and Chang, S. L., *J. New Engl. Water Works Assoc.*, **61**, 285 (1947).
(7) Ardern, E., and Lockett, W. T., *J. Soc. Chem. Ind.*, **33**, 523 (1914).
(8) Sawyer, C. N., and Nichols, M. S., *Sewage Works J.*, 11, 462 (1939).
(9) McCabe and Eckenfelder, "Biological Treatment of Sewage and Industrial Wastes," Reinhold Publishing Corp., New York, Vol. 1, Chap. 1. **1956**.
(10) Sawyer, C. N., and Rohlich, G. A., *Sewage Works J.*, **11**, 946 (1939).
(11) Sawyer, C. N., *Sewage & Ind. Wastes*, **30**, 757 (1958).
(12) Buswell, A. M., and Mueller, H. F., *Ind. Eng. Chem.*, **44**, 550 (1952).
(13) Genter, A. L., *Sewage Works J.*, **13**, 1164 (1941).
(14) Genter, A. L., *ibid.*, **11**, 774 (1939).
(15) Sawyer, C. N., Frame, J. D., and Wold, J. P., *Sewage & Ind. Wastes*, **27**, 929 (1955).

Chem Ed

LETTERS

To the Editor:

Some Definitions

In these days we find in the press and over the radio many discussions concerning the subjects of science, mathematics, engineering, and education. Since nobody seems to be certain of what these terms mean, I am submitting the following definitions:

(1) Science is the entire body of verified knowledge pertaining to natural phenomena.

(2) Mathematics is a universal, symbolic language in terms of which relations among definable quantities may be expressed and by means of which, through logical processes, relations, not otherwise apparent, may be disclosed.

(3) Engineering is the art of applying science to constructive and, at times, destructive purposes.

(4) Education is a mental process through the operation of which one gains understanding.

CHARLES A. KRAUS

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To the Editor:

I should like to commend Professor Robert D. Vold for writing and the JOURNAL OF CHEMICAL EDUCATION for publishing "Technical Education and Development in an Indian Environment," October issue, pages 522–26. In my opinion, this is a paper with a rare combination of qualities: a thoughtful contribution to the philosophy of chemical education, first-hand information on chemical technology, economics and international politics in an interesting foreign country, and, above all, consideration of human values and Christian principles. In addition to unusual content, it is written in a very readable and scholarly style. I urge any readers who missed Professor Vold's article to look it up and enjoy it. May we have more contributions on as high a level.

F. C. STRONG III

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To the Editor:

In the article by Marion (J. CHEM. EDUC. **34,** 441 (1957)) N,N-diethyl paraphenylenediamine is used as dye coupler in the color developer for Anscochrome Color Films. This may be substituted to advantage by "Genochrome," a derivative of diethyl paraphenylenediamine made by May and Baker. When substituting the sodium bisulfite by potassium metabisulfite the composition of the color developer will be as follows:

Genochrome	2.40 g
Sodium carbonate, monohydrated	31.0 g
Potassium metabisulfite	0.55 g
Potassium bromide	0.5 g
Water to	500 ml

This developer is more stable than the one compounded with diethyl paraphenylenediamine.

The results obtained with *dimethyl* paraphenylene diamine (B.D.H.) as a dye coupler are not very satisfactory because the colors become weak and greenish. The first objection is met by using concentrations of the dimethyl derivative and the potassium metabisulfite which are 50% higher than the concentrations mentioned by Marion. By doing this the colors are still greenish but the lines become better defined. By using a mixture of the methyl and ethyl derivative, this advantage holds and the excess of greenish colors disappears. The following composition of the color developer is recommended:

Genochrome	1.20 g
N,N-dimethyl paraphenylenediamine	1.50 g
Sodium carbonate, monohydrated	31.0 g
Potassium metabisulfite	0.69 g
Potassium bromide	0.5 g
Water to	500 ml

Some people may judge the colors too bluish when using either the Genochrome developer mentioned first or the one mentioned by Marion. This objection may be met by diminishing the concentration of the dye coupler and the potassium metabisulfite. In general, a decrease of about 5% will be sufficient. However, in this case the lines appear to be less sharp. More potassium bromide (50 mg) in the first developer will correct this.

In some cases it may be advantageous to develop at a higher temperature. At 23.0°C a time of development of 12.0 minutes for the first developer and 11.5 minutes for the color developer has proved to be satisfactory. The timing of the other operations need not be changed.

In the original article, sodium bisulfite is mentioned in the composition of the bleaching bath. This has to be sodium bisulfate.

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Chem Ed

BOOK REVIEWS

Standard Methods of Clinical Chemistry. Volume 2

The American Association of Clinical Chemists. *David Seligson*, Editor, University of Pennsylvania, Academic Press, Inc., New York, 1958. xii + 217 pp. 16 × 23.5 cm. $5.50.

Like the first volume in the series, which was published in 1953, the current volume consists of thorough presentations of modern methods for analyzing blood, urine, feces, and other biological materials for clinically significant compounds or elements or for performing empirical tests which indicate the functioning of certain organs. The book is intended primarily for professional clinical chemists, but should be of use to medical technicians, pathologists, and others whose vocations are related to clinical chemistry. The style is clear and easily read; there are very few errors of any kind.

For each method, there are given: (1) the historical background; (2) the principles involved; (3) a list of all reagents required with detailed directions for their preparation and procurement; (4) step-by-step procedures with explanatory notes; (5) the precautions necessary to insure the highest accuracy and precision; (6) all calculations and standardizations involved, and (7) a thorough discussion of the clinical significance of the results, with normal ranges and, where pertinent, the influences of various physiological factors (such as age) on the normal values. In most cases, the relative merits and failings of the methods are also discussed. The calibration of photoelectric colorimeters, the operation of sensitive *p*H meters, and the operation of a flame photometer are also included. An extensive list of references, both specific and general, is appended at the end of each chapter. Reasonably complete author and subject indexes are provided at the end of the book.

With the exception of two (blood *p*H and flame photometry), each method has been checked independently by at least one clinical chemist in addition to the person submitting the procedure. In most cases, values obtained in two or three laboratories by analyzing several known and unknown samples are given, providing adequate bases for evaluation of the precision and accuracy of the method. Similarly, data comparing the results of analyzing the same samples by two different methods are presented.

Although eight of the methods require expensive equipment, such as a Beckman DU spectrophotometer, a flame photometer, or a fluorometer, the majority can be done with a minimum of special equipment. The large number of explanatory or precautionary notes and suggestions, together with the data indicating the accuracy and precision, should make even the more complicated procedures workable for relatively inexperienced technicians who have had adequate training in the fundamentals of clinical chemistry.

Although the methods given for the determination of cholesterol have much to commend them, this reviewer has found the $FeCl_3$-H_2SO_4 method of Zlatkis and Boyle to be accurate and convenient. Comparative data might well be given in the next volume of this series.

The brief discussion, on page 104, of the relative clinical significance of blood urea nitrogen (BUN) and nonprotein nitrogen (NPN) levels fails to point out that since the normal value for BUN is only half of that for NPN a moderate retention of urea will be much more evident if BUN is determined, because the relative increase from the normal will be much greater. Similarly, in some conditions a rise in one component of the NPN will be counterbalanced by an equivalent decrease in another, preventing any significant change in the NPN value.

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Textbook of Biochemistry

Benjamin Harrow, Emeritus Professor of Chemistry, and *Abraham Mazur*, Associate Professor of Chemistry, City College, New York. W. B. Saunders Co., Philadelphia, 1958. ix + 557 pp. 106 figs. 79 tables. 16 × 24.5 cm. $7.50.

This is the seventh edition of a textbook which has been popular for many years. Numerous changes have been made to bring the book more nearly up to date. It is concerned primarily with human physiological chemistry, the descriptive "biochemistry" of medical school tradition, and as such it will no doubt continue to enjoy wide acceptance. Its organization follows the historic pattern, beginning with elementary carbohydrate chemistry, followed by descriptive chemistry of other naturally occurring compounds, enzymes, the physiology of digestion and absorption and blood, chemical reactions in metabolism, nutrition, tissues, urine, etc. The treatment is compact, and excellent in many ways. The seventh edition, in recognition of the importance of reaction kinetics and thermodynamics in biochemistry, contains several new ventures into the field of physical chemistry. Unfortunately, the presentation is marred by simple errors.

On pages 119–120, it is assumed that first-order kinetic behavior always indicates a monomolecular reaction. Curiously, the one example given to illustrate a monomolecular reaction is admitted in the very next sentence to be in fact a bimolecular reaction (hydrolysis of sucrose).

Contrary to the statement on page 133, the law of conservation of energy is not the second law of thermodynamics. Beginning with the following equation, not derived:

$$\Delta F = \Delta F^\circ + RT \ln [(C)(D)/(A)(B)] \quad (1)$$

the authors go through what is intended to be a derivation of the equation:

$$\Delta F^\circ = -RT \ln K \quad (2)$$

This "derivation" does not seem valid for a number of reasons, among them being the fact that equation (1) was itself derived from previous knowledge of the relation in equation (2). The fact that

Reviewed in This Issue

David Seligson, Editor, Standard Methods of Clinical Chemistry. Volume 2
Benjamin Harrow and *Abraham Mazur*, Textbook of Biochemistry
F. Wild, Characterisation of Organic Compounds
George J. Janz, Estimation of Thermodynamic Properties of Organic Compounds
Friedrich Klages, Lehrbuch der Organischen Chemie. Band 3
Malcolm Dixon and *Edwin C. Webb*, Enzymes
Frank A. Bovey, Polymer Reviews. Volume 1: The Effects of Ionizing Radiation on Natural and Synthetic High Polymers
Harold H. Strain, Chloroplast Pigments and Chromatographic Analysis
Proceedings of the Congress on Modern Analytical Chemistry in Industry
K. W. Bagnell, Chemistry of the Rare Radioelements
Max Hansen and *Kurt Anderko*, Constitution of Binary Alloys
Frederick R. Eirich, Editor, Rheology: Theory and Applications. Volume 2
Fritz Feigl, Spot Tests in Inorganic Analysis
Paul Pascal, Editor, Nouveau Traité de Chimie Minérale. Volume 4

the "derivation" ends with "the right answer" is a phenomenon which is frequently observed in derivations on student examination papers. As Leibniz said, "le vrai peut être tiré du faux." The phrase "steady state" should probably read "standard states."

Page 134 implies that, without having any information as to the actual concentrations (or activities) existing within a system, one is able to know whether the system is to the left or the right of equilibrium, from the sign of $\Delta F°$. This would be as much a miracle as determining, from the horsepower of a man's automobile, whether he is about to set out on a trip or has just returned from one. As applied to exergonic and endergonic conditions, this confounding of $\Delta F°$ with ΔF of a reaction unfortunately occurs in many biochemistry textbooks.

Errors of the sort cited are not limited to this particular textbook of biochemistry. The widespread continued use by teachers of biochemistry of textbooks which perpetuate such errors does not speak well for present standards of classroom instruction in biochemistry. The presence of such errors is the more difficult to explain in view of the ready accessibility of elementary physical chemistry textbooks in which these subjects are presented correctly.

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Characterisation of Organic Compounds

F. Wild, Research Chemist, Department of Medicine, University of Cambridge. Cambridge University Press, New York, 1958. Second edition. viii + 306 pp. 15 × 22.5 cm. $6.50.

The second edition of this well-known book is identical with the first edition (1947) with the exception of the listing of some new derivatives with their physical constants and the revision of a number of melting points.

Six lines on the bottom of page 32 have been omitted and are supplied here from the first edition for those purchasers lacking the earlier volume:

> "...at a rate sufficient to keep the solution at 40°. After the final addition the solution is heated on a water-bath until a solid mass separates. The mixture is cooled to 0° in an ice-bath, and concentrated nitric acid diluted with water (10%) is added slowly until the reaction mixture is yellow. More solid is deposited during the addition of acid which is controlled so that the tem—...."

This book is devoted almost exclusively to derivatization; other subjects usually discussed in qualitative organic texts such as separation of mixtures, determination of physical properties and the relationships of structure to physical properties are treated lightly. There is no discussion of, or directions for, the qualitative detection of elements—it being assumed that the student is already familiar with this procedure.

The tables include various types of derivatives not found in the usual qualitative organic text.

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Estimation of Thermodynamic Properties of Organic Compounds

George J. Janz, Department of Chemistry, Rensselaer Polytechnic Institute. Academic Press, Inc., New York, 1958. ix + 211 pp. 16 × 23.5 cm. $6.

This book covers its subject matter, as indicated by its title, in two parts.

Part I, called Methods of Estimation, consists of eight chapters: 1. The Free Energy Change in a Chemical Reaction; 2. Thermodynamic Properties of Simple Polyatomic Systems by Statistical Thermodynamic Methods; 3. Thermodynamic Properties of Long Chain Hydrocarbons; 4. The Method of Structural Similarity; 5. The Methods of Group Contributions; 6. The Method of Group Equations; 7. Heat of Formation and Heat Capacity; 8. Applications of the Thermodynamic Method.

Part II, called Numerical Data, consists of 48 tables of the data needed to make the calculations described in Part I. These calculations are not only described in Part I, but many well-chosen examples are provided.

The book is well written, well organized, and much needed. When the reader overcomes his irritation at certain minor defects, such as the use of the misleading and long-discredited term "heat content" (instead of "enthalpy" or "total energy"), he will become enthusiastic about the excellent job the author has done.

Every library of a college or university, every chemistry department, every teacher of physical chemistry or thermodynamics, and every graduate in chemistry or chemical engineering should own this book.

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Lehrbuch der Organischen Chemie. Band 3

Friedrich Klages, Professor of Organic Chemistry, University of Munich. Walter de Gruyter & Co., Berlin, 1958. xix + 766 pp. 31 figs. 24 tables. 17.5 × 24.5 cm. DM 62.

The title of the book could be freely translated as "Selected Topics in Organic Chemistry." The author's intention, as stated in the Introduction, was to give to the reader..."a deeper understanding of the many relations and connections between the various compounds and classes of compounds which are often more important than the individual facts to a still learning chemist." The present work is a third volume of a "Textbook of Organic Chemistry" and the reader is assumed to be familiar with the basic concepts and theories of organic chemistry which are presented in the first and second volumes. However, the discussions are so clearly written and so richly documented with references to original (mostly German) literature that references to the first two volumes are only very rare. The chief advantage of this book over its few American equivalents (e.g., "Organic Chemistry, An Advanced Treatise," H. Gilman, Editor) is the fact that all the chapters were written by only one author who achieved a rather remarkable didactic unity in discussions of seemingly unrelated subjects. The work was meant primarily to be a guide to a student who was already familiar with the principles of chemistry (graduate students and advanced seniors), but any practicing chemist will find the present volume an interesting and profitable reading. The printing, paper, and general typographical arrangement are excellent.

The chapter titles are: "Mineral" Organic Materials (coal, petroleum, etc.) (20 pp.); Organic Dyes (150 pp.); Polymer Chemistry (isotactic polymerization is not mentioned) (40 pp.); Carbohydrates (100 pp.); Isoprene Derivatives, Steroids (50 pp.); Fats, Phenols (30 pp.); Nitrogen Containing Natural Materials (proteins, pyrimidine derivatives and alkaloids) (180 pp.); Fundamentals of Biochemistry (physiologically active substances, enzymes, principles of metabolism) (130 pp.)

The book is warmly recommended to anyone interested in systematic organic chemistry.

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Enzymes

Malcolm Dixon, Reader in Enzyme Biochemistry, and *Edwin C. Webb*, Lecturer in Biochemistry, both of the University of Cambridge. Academic Press, Inc., New York, 1958. xxxiii + 782 pp. Many figs. and tables. 16 × 23 cm. $16.

Haldane's "Enzymes," first published in 1930, it is safe to say, has been regarded with affection and respect as a model of a critical treatment of theoretical enzyme chemistry. However, with the passage of time and with the rapid proliferation of both descriptive and theoretical enzymology the book has become more venerated than used. This reviewer has not been alone in often having thought how gratifying it would be were Haldane to turn again his intellect and skill to this subject, now that it has grown out of its infancy. Haldane apparently has not chosen to return to this task, but the present treatise by Dixon and Webb well fulfills this wish.

The present book, as of the moment, is the only one available which offers a critical and reasonably comprehensive exposition of enzyme principles. Al-

(*Continued on page A100*)